

THE MANUFACTURE  
AND COMPARATIVE MERITS OF  
WHITE LEAD AND ZINC WHITE PAINTS



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*TRANSLATED FROM THE FRENCH*

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## TRANSLATOR'S PREFACE

POLEMICAL parts of this book form a contribution to a controversy which is being carried on as vigorously in France and other continental countries as in the United Kingdom and the United States. It is hoped that English-speaking combatants will find here some valuable ammunition for their warfare. Many painters will agree with the author that white lead as a paint basis is unrivalled, even with the serious drawback of darkening under the action of sulphuretted fumes, and the danger from lead poisoning by reckless handling. With reference to Stas' saponification theory, it is well to bear in mind that linseed oil contains free fatty acid, which plays an important part in white lead paint. It must not be forgotten that it is for the advantage of those interested in inert white lead substitutes to claim that white lead is itself inert.

As to the practical portions of the work, especially the sections on paint grinding, the translator believes that they fill a somewhat conspicuous gap in our special literature of the subject. It will be noted that in the matter of packages French practice differs to some extent from our own. The application of stiff paint as an *enduit*, or continuous layer, to ensure a smooth surface, as done in France, is not

practised in Britain, except as far as "filling up" is concerned. Our only equivalent for the *endviseur* is our painters' labourer. It would be difficult to get such a thick layer as an *enduit* to dry in our climate.

DONALD GRANT.

LONDON, *October* 1907.





# THE MANUFACTURE AND COMPARATIVE MERITS OF WHITE LEAD AND ZINC WHITE PAINTS

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## CHAPTER I.

### THE FUNDAMENTAL PRINCIPLES OF PAINTING IN OIL.

A COAT of paint is applied, in the building and constructive trades, generally, with two objects in view. The first function which the coat of paint performs is to impart a predetermined colour to the object to which it is applied; the second function is to preserve that surface against the weather. Such a coating ought, therefore, to possess very special properties. It should be perfectly opaque, or, as is said in the trade, it should have such good *covering* power, as to hide completely the colour, natural or artificial, of the surface beneath it. It should be impermeable, so as to protect the surface against rain, when it is a question of outdoor work; and against condensed water, in the case of indoor work. Finally, it should be resistant, because in outdoor work it is exposed to the erosive action of the wind, dust, and rain; and in indoor work to the friction of scrubbing. Moreover, all these different properties should be obtained by the application of a very thin coat of paint, so that its application does not dis-

figure the surface, by filling up the hollows, and thickening the parts in relief.

Paint, ready to be applied by the brush, consists of a mixture formed by—(1) a basis or foundation intended to impart body to the paint. This basis may be either white lead or zinc white. (2) A coloured substance, in as fine powder as possible; it is generally an ochre, an oxide, or a metallic salt. (3) Linseed oil, or any other drying oil, which they are in the habit (in France) in the painting trade of terming, very improperly, *huile grasse* (poppy, œillete, sunflower, etc.). (4) The whole is diluted with a volatile oil, spirits of turpentine, which at the present day is often replaced by heavy benzols, or by white spirit (light petroleum spirit).

Each of these constituents plays an important rôle:—

(1) The basis or fundamental part of the paint ought to be perfectly white, so that the colour added to it to produce a certain tint or hue is in no way modified. This applies with the more force, as the necessity is greater to obtain very delicate and very fresh tones. The white lead industry, and the zinc white industry, having adopted the excellent practice of delivering these products, in the form of a paste in oil (stiff paint), the painter ought to be on his guard to see that this stiff paint is perfectly homogeneous, very finely ground, and neither of too firm nor of too soft a consistency. To determine the consistency of stiff paint, a sample is taken from the keg, or other vessel, in which it is contained, by a painter's knife. A sample should be obtained, which is cohesive, and terminates in a point. This point should be straight, and only slightly inclined at its drawn-out end. On the other hand, the hollow produced in the bulk of the paint in the keg should retain its shape, and only disappear in course of time or by jarring the keg. When the soft paste tends to flow from the knife, it is described by saying that it is "stringy," that is, it contains too much oil, and may

and less oleic acid. The mixed fatty acids which can be separated from good linseed oil are present in the mixture in the following proportions per cent. :—

	Per Cent.
Linolenic acid . . . . .	15
Isolinolenic „ . . . . .	65
Linoleic „ . . . . .	15
Oleic „ . . . . .	5
	<hr/>
	100
	<hr/>

On the face of it, there is nothing absolutely definite in this composition. It varies according to the source of the seed from which the oil was expressed ; it varies with the time that has elapsed since its expression from the seed, because, exposed to the air, the oil undergoes a rapid oxidation, which partially transforms the above acids. Everyone knows that the drying of linseed oil is not due to the evaporation of a volatile portion of the liquid, but to the absorption of oxygen, which transforms all the fatty acids into oxylinoleic acid ( $C^{16}H^{25}O^5$ ), which would appear to be the last and most stable term to which linseed oil can naturally attain. This oxidation goes on more rapidly in a warm atmosphere than in a cold one ; but a mild temperature should not be exceeded. Linseed oil, heated to about  $250^{\circ}$  C. ( $482^{\circ}$  F.), loses some of its drying power, although it becomes thicker when it is kept for a sufficiently long time at that temperature.

Oxylinoleic acid, prepared in quantity, forms a transparent, more or less dark yellow, resinous mass, endowed with a certain amount of elasticity. When a layer of oil, which dries naturally, is spread on a piece of glass, it is rapidly covered by a dry pellicle or skin, which is precisely due to the oxidation just being discussed ; but if the layer of oil be rather thick, the portion under the skin takes a rather long time to dry. This is due to the fact that the pellicle in question forms an

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obstacle to the passage of the oxygen of the air. The same thing occurs when the oil is applied in the form of paint, which further justifies the principle enunciated above of only applying paint in very thin coats. Oils which dry naturally have here been discussed intentionally, because oils are made in the trade, the drying propensities of which are considerably increased by boiling, for a greater or less length of time, with metallic oxide or salts. Of these latter the most generally used are litharge, red lead, peroxide of manganese and borate of manganese, dehydrated zinc sulphate (white copperas). The exceptional drying power of those oils, to which painters apply the general term "boiled oil," arises from the fact that there is produced, in their preparation, metallic salts of the above fatty acids, which rapidly solidify. These boiled oils often enter into the composition of paints—so as to increase the drying propensities of the natural or raw oil—in a proportion varying from 3 to 5 per cent. of the latter.

(4) The three ingredients, base, colour, and linseed oil, form the essential constituent elements of the paint; but, as it is the solid matter which gives the covering power, the oil being naturally transparent, even when dry, it ought to enter in a determined ratio in proportion to the amount of oil. But the paint so reduced is too thick to be laid on by the brush. It is therefore thinned by a volatile fluid, by means of which it is brought to the fluidity desired for easy working. When once applied, and spread out under the brush, this volatile matter disappears by evaporation, and the very thin layer of paint only contains the three elements above mentioned.

The liquid most generally used is spirits of turpentine, which, recently distilled, is a colourless liquid, possessing the characteristic smell of turpentine, and a density of 0.860; its boiling-point lies between 156° and 157° C.

When it boils above this temperature, the spirit has been sophisticated by the addition of rosin, or rosin oil, or, again, it

may be old spirits of turpentine. As it ages, it turns yellow, and thickens, forming what is called "thickened turpentine," *essence grasse*, which is endowed with special properties, but is not adapted for painting. The painter should therefore select a colourless and very fluid spirits of turpentine.

The less spirit of turpentine and more oil in a liquid paint the more brilliant is the resulting coat of paint, and the painting is said to be done with a good bodied paint (*detrempe grasse*); inversely, the more spirits of turpentine and less oil, the less brilliant is the coat of paint, and it is then said to have been painted with a poor bodied paint (*detrempe maigre*). Fine flat-surfaced paints are obtained by thinning down the stiff paint with spirits of turpentine alone. The paint then contains no oil but that present in the stiff paint, forming the base. But good bodied paints yield much better coats, as far as durability is concerned, than those formed by poor bodied paints.

It has often been proposed, especially when spirits of turpentine is dear, to replace it by heavy benzine, and even by petroleum spirit, but painters much prefer spirits of turpentine. The partisans of benzine and white spirit proclaim the superiority of these products, because their evaporation is more rapid, more complete, and without residue; whilst spirit of turpentine evaporates more slowly, and tends to resinify, in contact with the air, thus introducing a deteriorating agent into the paint. The partisans of spirit of turpentine attribute to it the property of accentuating the drying propensities of the oil, always of great benefit in painting. It follows in regard to this point, from numerous tests made by the author, that by using a good, recently distilled, spirit of turpentine, no deteriorating resinification will occur in painting therewith. Moreover, the resulting paints were easily applied, the brush gliding, as it were, of its own accord. With benzine and white spirit the paints had always the feeling of being too dry, and more hard to spread, this applying to paints made

normally as above. The author then thinned the paints with oils, thickened to a certain body, by boiling, and, in that case, benzine and white spirit did not show any difference from spirits of turpentine, either as regards application, or the durability of the resulting coats of paint. It seems, therefore, *ceteris paribus*, that the superiority of spirit of turpentine, lies in the greater facility with which the paint can be applied, this liquid having, so to speak, greater unctuousity than the rivals opposed to it. Thus, in using the latter, it is necessary to watch the proportions in which they are made to enter into the paint, so as to leave therein an unctuousity corresponding to that which would result from the use of spirit of turpentine.

Paint is generally prepared by grinding the base in oil, the colour is then incorporated, and, finally, spirit of turpentine is added to bring about the desired fluidity. The paint is said to be thinned. If a brilliant paint be desired, the proportion of oil to spirit of turpentine is increased; if the coat of paint should be very brilliant, raw oil is mixed with the boiled oil, and, reciprocally, less spirit of turpentine is used. To obtain flat coats, the stiff paint is thinned with spirits of turpentine alone, or with very little oil.

Strictly definite proportions for producing perfectly good liquid paint cannot be given. Each of the elements of which it is composed not only vary at the will and with the skill of the practitioner, but vary also with the nature of the materials placed in mutual contact. It has just been said that the ratio of oil to spirit of turpentine varies with the degree of lustre which it is desired to obtain; if, on the other hand, the bases most generally used, white lead and zinc white, show only slight, almost inappreciable, differences from one factory to another, it is not the same with the tinting colours, which not only exhibit great differences amongst themselves, but also differ according to the firm from whom obtained. These products can be obtained in variable molecular conditions.

Now this physical property has a great effect on painting materials. It is perfectly well recognised that for any given powder, the lower its apparent density the greater will be its spreading power, and the more oil it will require to form a paint of a given fluidity. Thus, as far as products made by precipitation are concerned, this density may vary almost infinitely, which explains why a certain product may require a "thinner" more or less rich in oil. That is, moreover, the rationale of the methods of working of those painters who, when they thin paints, never do so by weighed quantities, but only by volume, which they gauge by the eye. Whilst admitting that there are many cases where it would be difficult to work otherwise, it is a matter for regret to see this operation conducted in such an empirical or rule-of-thumb way, even with products possessing perfectly constant physical properties, such as the bases white lead, zinc white, and a good number of tinting colours.

This chapter may well be closed by a few remarks on driers, which are almost always added to paint. As the name indicates, driers are intended to hasten the drying of the raw oil entering into the composition of the paint vehicle. The driers used in painting are of two sorts—liquid driers and siccatives in powder. The first is formed from oil, boiled with a salt of lead or of manganese, and generally thinned with a greater or less amount of spirits of turpentine. When paints are intended for application in localities, where they may be exposed to sulphuretted hydrogen emanations, the use of lead driers should be forbidden, so as not to blacken the paint by the formation of lead sulphide. Manganese driers are used in such cases.

Solid driers, generally termed "zumatic driers," (siccatives), are made by the intimate mixture of an inert, pulverulent product, such as carbonate of lime and finely pulverised litharge, or of dry white lead. As siccatives of this category are liable to blacken under the action of sulphuretted hydrogen, lead driers

## FUNDAMENTAL PRINCIPLES OF PAINTING IN OIL 9

are replaced by manganese driers, and principally by borate of manganese. Driers are added to the paint, in minimum proportions, in the ratio of 3 to 5 per cent. of the raw oil which they contain. Certain painters lower even this figure by using the same proportion calculated to the whole paint.

Liquid driers ought to be preferred to driers in powder form, because their admixture with the paint is far more intimate, and consequently more uniform. Paints with a white lead base and the tinting colours of which are also lead salts, such as lead chromate, red lead, etc., require no driers, being sufficiently drying in themselves.

## CHAPTER II.

### THE DIFFERENT VARIETIES OF WHITE LEADS.

#### THE DUTCH PROCESS—GRINDING WHITE LEAD IN OIL.

WHITE lead has for a long time been the exclusive basis of all oil paints, in virtue (1) of the body which it imparts to the paint, (2) of the drying property which it imparts to the oil, and (3) of the resistance which it presents to the action of atmospheric agents. It was known in the most remote antiquity. The Greeks and the Romans knew how to prepare it. After them the Arabs produced it successfully. But the cradle of its industry would appear to have been Venice, which for a long time had the monopoly of its manufacture, whence it passed into Austria, into Holland, into England, and finally into France, where its preparation did not assume a manufacturing scale until the beginning of the nineteenth century.

White lead is a salt of lead, which is too often wrongly regarded as a carbonate of lead. It is really a hydrocarbonate of that metal, with the formula  $2\text{CO}_3\text{Pb}, \text{PbOH}_2\text{O}$ ; however, this formula must not be taken but in an altogether general sense, for it corresponds to the product with the composition of 31 per cent. of hydrate to 69 of carbonate. Whereas these proportions not only vary from one process of manufacture to another, but the proportions even vary in white lead made by the same process; by the Dutch process, for example, from one operation to another, white leads are obtained con-

taining 26 to 35 per cent. of hydrate, and 65 to 74 per cent. of carbonate. Whatever be the method of manufacture, the goal aimed at is always to obtain the salt of lead which corresponds to the above formula, variations excepted, within the indicated limits of the percentage of the two constitutive elements of white lead. Many processes are in existence for the production of white lead yielding products of rather variable quality. They may be classified as follows:—

1. *Dutch process*.—This is by far the most generally used in white lead producing countries, and particularly in France, because it yields quite a superior product for painting, principally with regard to covering power. From the fact that this process yields an excellent product, it was for a long time believed, and is still frequently believed, that the best white lead comes from Holland. That is a grave error, for French manufacturers produce white lead which can compete with the best brands of the whole world, whilst, on the other hand, the small amount of white lead made in Holland is of inferior quality, being almost always sophisticated with sulphate of baryta.

2. *The French or precipitation process*, more generally known under the name of the Clichy process, was invented by Thenard in 1801. This process has never given but a secondary quality of white lead, in spite of the important improvements which have been successively brought to bear on the method. Moreover, the few factories using this method likewise make white lead by the Dutch process, and always sell this latter at a higher price than the white lead they make by the Clichy process.

3. *Hot chamber process*.—This method, very common in Germany, is a variation of the Dutch process, in which the natural heat disengaged by fermenting farmyard dung is replaced by artificial heat from a fire. The white lead thus obtained is good, but less esteemed by the painter than white

lead by the Dutch process, in spite of the fact that it is generally of a purer white than the latter.

4. *Krems process*.—This is another variation of the Dutch process. As its name indicates, it was first adopted at Krems, from which it spread through Austria into Germany. The heat produced by fermenting farmyard manure is replaced by that generated by the fermentation of the *marc* of wines (grape skins, etc.). The white lead thus produced is very good, it is of a particularly brilliant white; it is still often termed Krems white in trade. In Austria, where this method is very well conducted, the finest scales of white lead are selected to form quite a special quality, known under the name of *silver white*, which is used in fine painting.

5. *English method*.—This process is based on the simultaneous action of acetic acid or lead acetate, and carbonic acid on litharge. A rapid method of manufacture is thus obtained, but the white lead which results is less dense, covers less, and is, consequently, less appreciated than that furnished by the Dutch process; the latter process, therefore, seems to be the most generally used even in England.

#### DUTCH PROCESS.

This process, being by far the most general one, it will be described in some detail. It rests on the following principle: Metallic lead submitted to the combined action of the air and of acetic acid forms a basic acetate, which, in presence of carbonic acid, yields hydrocarbonate of lead and neutral acetate of lead; this latter is decomposed to a great extent by the moist carbonic acid produced by the fermentation of organic matter—farmyard dung, spent tan, wine marcs (*grape skins*), and often by a mixture of these different materials. This fermentation produces a temperature which may reach 80° and even 100° C. (say, 176–212° F.).

As to the industrial application of this principle, an applica-



tion which has not, with the exception of a few details, varied for over a century, it comprises the following operations:—(a) the preparation of the lead to be converted; (b) building the stack; (c) the management of the stacks during the progress of the conversion; (d) dismantling the stacks.

*Preparation of the lead.*—The lead is converted either in the form of sheets or gratings. The latter is the form most frequently adopted, because it exposes a larger surface of the metal to be attacked. The lead used should be of premier quality, and preference is generally given to soft refined. If sheets be used, the sheets are cut up into pieces of about 50 to 60 centimetres in length (say, 20–24 inches) by 10 to 20 centimetres in width (say, 4–8 inches), and 2 centimetres thick (say,  $\frac{3}{4}$  inch). If the lead be used in the form of gratings, it is melted in a hemispherical pot, about 40 inches wide, and it is run into moulds having the form of the gratings which it is desired to obtain.

The melting should be conducted in such a way that the lead fumes, very feeble it is true, which may be disengaged, the lead being at the temperature of about 400° C. (752° F.), do not incommode the workmen. The melting-pot is therefore placed under a hood with a good draught; some factories even push this hygienic measure so far as to instal a fan above the hood to propel the vapour in question a long way off into the open air. It is a very laudable precaution, the adoption of which cannot be too strongly urged.

*Erecting the stacks.*—The stacks or pits constitute the apparatus in which the chemical reaction is produced, namely, transformation of the metallic lead into hydrocarbonate. A stack consists of a rectangular excavation made in the soil to the depth of about 5 feet, and is continued above ground by solid walls in masonry to the height of about 10 feet. On the front of the stacks the wall does not entirely cover that side, so as to leave a free passage for building the stack.

As to the superficial dimensions given to the stacks, they vary somewhat in different factories, being about 16 feet in width, with a length of 16, 32, and 48 feet.

In building a stack, the workmen entrusted with the job first spread a layer of farmyard dung on the floor, 40 centimetres (say, 16 inches) thick, then on that layer they arrange glazed earthenware pots containing dilute pyroligneous (acetic) acid marking 3° B. If sheets of lead are used, they are introduced into the pot, the interior of which is so shaped that the lead does not come in contact with the acid, and the pots are themselves covered with a disc of lead forming a lid; if lead gratings be used, they are simply placed on the pots, the one above the other. In both of these arrangements, the pots are placed the one against the other, and thus cover the whole surface of the bed, leaving simply, between the sides and the first range of pots, an open space of 16 inches, which is filled with dung.

A first bed or layer of pots being thus made with lead, in sheet or in gratings, cross-beams are placed above it, and these support, in their turn, a floor of boards covering the whole of the surface of the pots. On this floor another layer of dung is made as in the bottom of the stack, on which is installed a new bed or layer of pots, lead, cross-beams, and boards, as made in the sole of the stack, and so on until 8, 9, or 10 superimposed rows of pots are built up. The bay of the wall, leaving passage to the workmen who built the stack, is closed up, and the stack left to itself; it is, be it well understood, finished off on the top by a layer of farmyard dung.

Finally, it must be mentioned that in building up the stack a chimney is formed in the centre, to carry off the vapours. This arrangement of the stacks corresponds well, it will be seen, with the principle of the reaction, which has to be brought into play. The heat, disengaged by the fermentation of the dung, causes the acetic acid contained in the pots to

evaporate, and these vapours, concurrently with the air stored between the floorings and the pots, attack the lead at the same time that the carbonic acid, also disengaged by the fermentation of the dung, fixes itself on the basic acetate, so as to produce hydrocarbonate of lead.

*Note.*—The factories which still work with lead sheets use a pot of a special shape. In the interior of the latter, and half-way up, there is a circular rim, on which lies the sheet of lead, rolled into the form of a spiral, whilst the dilute acid, placed in the bottom, rises up to within a few centimetres of the above-mentioned rim. These pots generally have the following dimensions:—depth, 24 centimetres (say, 10 inches); top diameter, 15 centimetres (say, 6 inches); bottom diameter, 10 centimetres, (say 4 inches). With their somewhat rounded shape, they somewhat resemble laboratory crucibles.

When the lead is in gratings, and that is the most general form in the white lead works of the present day, the pots are absolutely uniform in the inside; and their depth is only about half, say about 12 centimetres (say, 5 inches). Their capacity then is still amply sufficient for what acid they have to contain, the latter not filling them completely.

The conversion of the lead is so much the more complete the less the weight of this metal on the pots, in other words, per square metre of the surface of each of the beds in the stack, but the latter would then assume enormous dimensions, thus necessitating vast working space. To economise space, therefore, the pots are covered with several intercrossed gratings; and, it may be stated, in a general way, that there is introduced into the stack, on an average, double the weight of lead to that which corresponds to the chemical reaction which it is sought to accomplish.

The farmyard dung employed should be horse dung, and it is necessary to avoid that of carnivorous animals, such as the pig, for example. Such dung disengages sulphuretted hydrogen,

forming black lead sulphide. Horse dung itself, also, it is true, disengages sulphuretted hydrogen, but in such a small quantity as not to injure the whiteness of the white lead; moreover, many white lead manufacturers assert that the traces of lead sulphide thus produced impart to the white lead a more considerable covering power than when it is absolutely exempt therefrom. The dung can be used twice; it is preferable, however, to mix a portion of that previously used with fresh dung. Farmyard manure is to-day, to a large extent, replaced by spent tan, the process coming, it is said, from England; this product has many merits. (1) It is a more appropriate substance, and more hygienic for the workmen entrusted with building up and dismantling the stacks. (2) As it disengages no trace of sulphuretted hydrogen, it always yields a very white white lead. Finally, the exhausted tan can serve as fuel, in white lead factories, in furnaces specially constructed for its combustion. On the other hand, the fermentation of spent tan being much less active than farmyard dung, the work of the stacks last, with the first, two and three months, whilst, with the second, it is finished at the end of six weeks.

Again, in some white lead factories, the work is done with a mixture of farmyard dung and spent tan, with the view of profiting from the advantages accruing from the use of both these products. The author does not believe that this method of working is to be recommended, but that it is better to adopt exclusively one or other of these substances. Fermentation is always more homogeneous, and the working of the stacks more uniform.

*The working and management of the stacks.*—This is assuredly the most delicate part of the manufacture, and is generally only entrusted to an experienced foreman. It is by means of the chimney, arranged during the formation of the stack, that the progress of the reaction is regulated. The vapours are in

fact disengaged by this chimney, so the opening should be regulated so as only to let the vapour of water (*i.e.* steam) escape, and not to lose any pyroligneous acetic acid vapours. The interior temperature of the stacks should vary from 60° C. to 70° C. (140–158° F.) during the first three or four weeks; after this period the temperature lowers notably, and then, the chimney is completely closed. It is especially by the appearance of the vapour, which escapes, as well as its smell, that the white lead manufacturer recognises the good working of the operation; but this rule-of-thumb method is the cause of numerous mistakes, and the most experienced white lead manufacturers are not absolutely sure of their product until the stacks are dismantled and they may “spoil an operation,” in spite of all the care brought to bear upon it. By “spoiling an operation,” it is to be understood that the stack does not produce the desired quantity of white lead, and that the scales which it yields are neither white nor thick.

The exterior temperature likewise exerts a notable influence on the progress of the operation. It will be conceived that, in summer, fermentation is more active than in winter, and requires, therefore, to be followed with much greater attention. The yield is also better the less the quantity of metallic lead placed on the pots; but then the cost price is increased—(1) by the greater amount of space occupied by the stacks; (2) by the labour entailed in building them. Therefore the amount of metal per superficial metre of the stack is always forced, and it is taken that the latter transforms 40 to 60 per cent. of the lead with which it was fed, producing then 50 to 75 lbs. of white lead per 100 lbs. of lead treated.

*Dismantling the stacks.*—It may be said that the dismantling of the stacks is the converse of the building of them. It will only be necessary, therefore, to insist on certain quite special points of this operation, which are of particular interest as regards the health of the workmen. The dismantling of

a stack consists, therefore, in lifting off the upper coat of dung, the boarding, and the cross-pieces ; that done, the metal comes in sight, covered with a more or less thick layer of real scales, which constitute the white lead. At this stage of the dismantling process, the gratings covered with white lead are drenched with water so as to avoid the formation of white lead dust. Workmen, with hands covered by indiarubber gloves, raise the gratings, place them in wooden boxes, which are deposited in trucks or in small waggons to transport them to the adjacent workshop.

*Separation of the scales.*—As mentioned when discussing the yield, the gratings or sheets of lead are not entirely transformed into white lead. The metal is more or less deeply attacked, carrying, therefore, a more or less thick layer of scales ; but the core still consists of unconverted metal, which has to be removed. For that purpose, a mechanical process is adopted, which consists in passing the plates through a laminator with grooved rolls. Each white lead manufacturer possesses for this purpose *his machine*, more or less perfect, but which ought to fulfil the following requirements :—A workman with gloves on throws the plates covered with white lead, which he brings in the boxes above mentioned, into a bin. From this bin, the plates pass between the grooved rolls ; the lead is, in a sort of way, scraped, and falls on to a cloth, from which a second workman, also with gloves on, seizes it to throw it into a receptacle of some sort. This lead, remelted, is used to make new gratings and new plates. As to the white lead, it is transported, automatically, by the cloth into a chamber, from whence it is afterwards taken to pass through the grinding mills. The machine for stripping the lead should be connected with a fan, which removes all the fine white lead dust, so that the men, whether occupied in feeding the lead covered with scale into the machine, or, in freeing the band from the stripped metal, are not liable to come in contact with white lead dust.

Again, according to the method of manufacture, and the method of stripping, the white lead is separated with a larger or smaller quantity of comminuted dust. This dust must, therefore, be the object of special supervision, and be aspirated by fans, special to the places where it is formed, to be stored, immediately and automatically, in perfectly closed reservoirs.

*Grinding the white lead scale in water.*—Arrived at the point just indicated, the white lead is finished, as far as chemical reaction and separation from the white lead is concerned, but it cannot be put on the market in that form, and it must be reduced to a very fine powder. Hence the necessity of subjecting it to energetic grinding. This operation is conducted in stone mills, analogous to those used for grinding wheat into flour. The scales of white lead submitted to this grinding are abundantly moistened with water, so as to form a paste, and it is this paste which is fed into the mills. The formation of injurious dust is thus avoided. To obtain an impalpable powder, the white lead passes through several mills in succession. Certain factories repeat the operation eight times. Generally the paste, ground by the first mill, is seized by a conveyor of an appropriate form, which carries it to a second mill, from the latter the paste passes in the same way to a third, and so on, up to the last grinding apparatus. These mills, when the operation is well conducted, are adjusted so that each of them effects a finer and a finer grinding. It is often said of these mills that they are arranged in "cascade" form.

In the early days of the manufacture of white lead it was thought the workmen could be perfectly protected from white lead dust by the fact that the white lead was ground as a water paste. The observations of several manufacturers, careful of the hygiene of their staff, have demonstrated (1) that the splashes from the mills projected on the ground, and on the clothes of the white lead workmen, were not long in drying and forming the dust which it was sought to avoid;

(2) that during great heat the substance heated under the stones and a little water evaporated, with a characteristic odour of lead.

To obviate the first inconvenience, the mills should be completely enclosed, likewise all the conveyors carrying the substance to the next mill. To remedy the second inconvenience, it suffices to fix, above the cover of each mill, an appropriate aspirator and expeller of the vapours above the roofs of the factory, where they are lost in the open air without any inconvenience.

As it issues from the last mill, the white lead ground to paste takes two different directions, according to whether it is to be put on the market dry, or converted into stiff paint. It may at once be mentioned that it is in the latter form that its use is most developed, and it is in that form that most white lead manufacturers deliver it. Nevertheless, certain industries, such as enamel works, potteries, oil boilers, etc., require dry lead in powder, which obliges white lead manufacturers to produce a certain quantity, which, it may be stated once more, is quite a minimum one, compared to that which is delivered ground to a stiff paint in oil.

Moreover, certain manufacturers or colour merchants prefer to buy dry white lead in powder, and to grind it in oil themselves. They thus pass for manufacturers, give to their product a special mark, and can, at the will of their customers, mix their white lead with a larger or smaller amount of sulphate of baryta (barytes), thus forming different numbers or qualities.

The system of Customs duties between different countries, moreover, encourages the grinding of white lead in powder. Without entering into details, as to the Customs duties between France, Germany, Belgium, Switzerland, etc., it may be said that when these duties are five francs (four shillings) on the product ground on oil, they are only two to three francs (one



and sevenpence to two and fivepence) on the dry product. It follows that the German grinders, amongst others, often buy from French or Belgian manufacturers the excess of their production of dry white lead in powder, to grind it themselves. On their side, the French grinders go to the Germans. In each country the white lead manufacturers are thus forced to sell white lead in powder, as a raw material without a trade mark, and at small profit, in such a way as to leave a remunerative margin on the selling price of white lead ground in oil, without indication of origin. It will be seen further on, in regard to grinding white lead in oil, how white lead is ground into a dry powder.

*Preparation of white lead as a dry powder.*—White lead finely ground in water paste form, as it issues from the last mill, is deposited in the dishes placed in stoves heated by steam to a temperature of about 80° C. (176° F.). These stoves should be perfectly ventilated, not only to accelerate the drying, but to drive away the moist vapour which, as already mentioned, presents a very marked smell of lead, and thus forms a product very injurious to the health of the workmen entrusted with placing the dishes in the stove, and taking them out again.

After five or six days the product is perfectly dry, and in the form of cakes, rather hard but very friable, and of a peculiar unctuousity to the touch. These cakes must be pulverised. They are taken by a workman, who reverses the dishes into a hopper, at the bottom of which is a screw conveyor, which, whilst crushing the material, carries it to a grinding machine.

As in the separation of the scales from their gratings, it is advisable to provide the hopper with a fan, which carries any white lead dust that may be formed far away from the operator.

As to the pulverising machines, the models in vogue are very numerous; they almost all consist of crushers, which revolve at great speed, in which the iron or steel blades energetically

strike the material so as to break up completely the agglomeration produced in drying, and to restore to the white lead the fineness which it had when in the state of water paste. Certain of these disintegrators are even fitted with sifting gratings, which only allow products of a certain degree of fineness to pass, whilst the tailings pass into a special receiver and are again passed through the disintegrator.

Without discussing the value of these machines, some of which work well, and yield a product of remarkable fineness, it may be safely asserted that one cannot be absolutely assured of a good final product, except by passing the powder furnished by the disintegrator through a sifting machine. This latter apparatus presents no very special feature. It consists, like all sifting machines, of revolving sieves, furnished with wire gauze of different numbers according to the degree of fineness desired, the tailings or core being again passed through the disintegrator. It need only be stated that the sifting machines should be perfectly close, and not allow any dust to pass through, and that the tailings should run into a special chamber, also closed, from whence an appropriate conveyor should carry them to the disintegrator. As, in spite of the precautions indicated, the sifting produces large quantities of dust, all spreading of such in the surrounding atmosphere is avoided by furnishing the sifting machine with an aspirator at the entrance and the exit for the material, or even on the body of the machine.

Sifting machines may be replaced by blowing machines, in which the force of the current of air entrains the white lead to the collecting chamber, where it forms a mass reduced to an impalpable powder. Blowing machines comprise fewer moving organs, and are generally made of wrought-iron, which admits of their being rendered absolutely hermetical.

It may be added that certain factories, that of M. Expert-Besançon, of Paris, amongst others, combine both pulverisation

and blowing in one machine. This apparatus is made of wrought-iron, and is absolutely tight; moreover, it has a strong aspirator, both on the feeding hopper and on the discharge exit; all air charged with dust, which issues from this aspirator, is propelled into a depositing chamber, where a steam-jet aids in precipitating the dust.

Finally, it may be stated that dry white lead is still delivered, in very small quantities however, in the form of cylindrical cakes resembling the sticks of chalk which are used in schools. This shape is got by pressing the water paste white lead and moulding it in the moist state, then drying in absolutely the same way as the cakes laid on the dishes.

Once dry, these cakes are arranged in boxes, or in any other form of package, and put on the market. It is well, it is even indispensable, that the workmen, on whom devolves the labour of insertion in the stove, and the withdrawal therefrom, should wear gloves during the whole time of handling. It is none the less advisable that packing be done in a well-ventilated place, or even under a hood fitted with a fan, which removes all the white lead dust, and propels it into a chamber, where it may be collected, to be added to the powdered white lead.

The packing of white lead in powder merits special mention. In a general way, this product is delivered in casks, and it is necessary that the contents be well packed. This is done by the use of presses, but here again it is necessary to take great precautions. Alongside the barrel being filled, it is necessary to arrange a hood, which, by means of a violent current of air, entrains the dust towards a depositing chamber, from which it is afterwards removed. In France this organisation is rendered somewhat difficult, because users of white lead in powder are accustomed to receive this product in casks of very variable net weight. In Germany, on the contrary, white lead manufacturers have adopted the excellent method of delivering white lead in casks of an absolutely

uniform weight and volume. It follows they can use mechanical filling, which, by suppressing manual labour, in great part, at least, avoids at the outset the dangers incidental to barrelling the lead. The French makers are, however, to be excused, as their production and their sale of white lead in powder constitutes a very small proportion of their production, 10 per cent. at the maximum. Ninety per cent. of their production is delivered in the state of a paste in oil (stiff paint), the preparation of which now requires to be examined.

#### GRINDING WHITE LEAD IN OIL.

The painter, who is the largest consumer of white lead, has been accustomed for a long time to use this product ready made, that is to say, combined with a certain amount of oil, which converts it into a stiff paste, that can be taken up by the knife without the paint either running, or "stringing," to use the trade term. Up to the middle of last century, this paste was made by mixing dry white lead in powder with a certain amount of oil, preferably linseed oil, which dries best. As already mentioned, there are a somewhat large number of paint manufacturers who buy white lead in powder, grind it in this state with oil, and sell it in the state of paste (stiff paint), either under their own name, with a distinct trade mark or brand, or without name or brand.

The grinding in oil of white lead comprises two operations—(1) mixing; (2) grinding.

1. *Mixing*.—Mixing consists in incorporating with the dry white lead a certain amount of oil, generally 90 parts of dry white lead in powder, with 10 parts of oil. The incorporation is effected in a mixer. In principle this apparatus consists of a cylinder of cast-iron, or of strong wrought-iron (body of the pug mill), in the centre of which there revolves a vertical shaft fitted with helicoidal blades, which not only keep the matter in motion, but, moreover, bring it from the centre to the periphery, by causing

it to assume a turning motion, in the same way as the sock of a plough in ploughing. The cylinder or body of the pug, which is fixed, is often fitted with internal baffles, consisting of iron rods projecting almost as far as the shaft. These baffles fixed to the side of the cylinder are placed between the movable blades in such a way that the material brought by the blades strikes against the baffles and is stopped there. The next blade seizes the slices thus produced, carries them farther on, where they are subjected to the same treatment, causing perfect mixture of the oil and powder. This apparatus presents a great analogy with a cement mixer (pug mill), only it is not so long.

Mixers are vertical or horizontal; when vertical, their bottom is often slightly rounded, and it is scraped by a helical blade bringing the matter from the centre to the periphery (circumference). A discharge door is fixed to the bottom of the machine, and, when opened, the matter in the state of paste, runs out naturally, by the effect of the lower blade. The orifice of the door is fitted on the outside with a sort of gutter, in cast-iron, which conducts the stuff towards a tub, or any other vessel, when it is run out, as just mentioned.

Mixers are also made horizontal; the cylinder (or body) is then horizontal, as well as the shaft fitted with blades. The latter only is movable. A charging door is fixed on the upper part of the cylinder, and in its lower part is a discharge door, from which the matter runs out by its own weight.

Horizontal mixers exhibit the most varied arrangements. There thus exist models much in use, the fixed cylinder of which is divided along a certain diameter into two parts. The top part opens to receive the material, the under part can also be entirely opened to discharge the apparatus. As these machines are generally very bulky, each of the movable parts, charging door and discharging door, is fitted with a counterpoise, in perfect equilibrium with the movable piece, to render manipulation easy.

What one should seek for in a mixer is the arrangement enabling the contact of two materials, so essentially different, in nature and density, as white lead and oil, to be renewed every moment. Thus the author is a great partisan of machines the work of which, if he may so express himself, is as irregular as possible. In fact, when the apparatus works regularly, as soon as the product being treated has assumed a pasty consistency, the movable organs force a way through this paste, and revolve without forcing the material to change its position, consequently without mixing the whole mass. Mixers, with blades in the form of a helix, especially when they are furnished with fixed baffles, exactly avoid this inconvenience.

It has been attempted to apply the principle of the mechanical kneader or masticator, with blades of a special shape to the mixing of white lead with oil, but the working of these machines is too regular, and it is always the same "furrow," so to speak, of pasty white lead which is being "ploughed," the rest of the mass remaining attached to the sides. The vertical mixer, in which the shaft armed with blades not only turns on itself, but describes a circular motion round the whole cylinder, has likewise been recommended. The apparatus designed so to act is very ingenious, but if it does good work, its output is less, owing to the greater length of path to be traversed by the parts in motion.

Whatever kind of mixer be used for the purpose of mixing dry white lead with oil, there are some necessary precautions to take at the time the mixer is charged with dry powder, which tends to diffuse through the surrounding atmosphere. Two methods are utilised to obviate this grave inconvenience. The mixer, especially when it is a vertical one, may be covered with a jacket of supple leather, or any other absolutely impermeable fabric. At the time of charging the mixer, this jacket, which completely envelops the cylinder body of the

mixer, can envelop, at its other extremity, the cask containing the white lead in powder. By tilting the cask, all the powder runs into the mixer, without generating dust outside. The jacket is not taken off the cask until some time afterwards, when it is judged no more dust will be raised by lifting off the cask. The mixer, as far as it is concerned, remains closed by this jacket.

The second method consists in placing the mixer, under a hood, in which a good fan is at work. The mixer can then be charged by means of a shovel, all the dust being aspirated and drawn into a depository chamber.

The mixer, being gradually charged with white lead in powder, there is then poured on it, either gradually, or all at once, the amount of oil necessary to convert the white lead into stiff paint. The oil used in France is linseed oil, or poppy oil, and principally the latter, as will be seen further on. As to the proportions in which this mixing is made, they are generally the following:—90 per cent. by weight of white lead, for 10 per cent. by weight of oil. Linseed oil is especially used when dry white lead in powder is being ground; the only plausible reason for this is that linseed oil is always considerably cheaper than poppy seed oil. Some manufacturers justify this preference, by saying that as linseed oil dries better than poppy seed oil, the stiff paint itself also dries better. If the above reasoning be correct, the motive is superfluous, for white lead communicates to the oil very quick drying properties, and it is useless, or almost so, that the latter should dry very well by itself. Further, if the linseed oil dry very rapidly, such as very old tanked oil, or oil oxidised artificially, it gives birth to a paint which, to use the trade term, “strings,” that is to say, is somewhat fluid. The consistency (degree of stiffness) of stiff white lead paint ought to be such that it can be taken up by the knife, and form on the latter a slice without seams or droppings. “Stringing” stiff paint may be avoided with the

above oils, by diminishing the proportions given. Finally, another inconvenience of linseed oil is to yield a white lead paint, which, applied alone, turns yellow somewhat rapidly, especially if the object to which the paint is applied is in the shade.

The fact of this yellowing furnishes a very good means of ascertaining whether the white lead has been ground in linseed oil, or in poppy seed oil. The white lead to be tested is spread on a glass slab or on a strip of tinned iron, which is supported against a wall, sloping it, so that it does not touch the wall. After a few days, the white lead is dry, and, if it be examined, it will be observed to have a very decided yellow cast, if prepared from linseed oil; it will, on the contrary, appear white, if made from poppy seed oil.

What has been said of the defects of linseed oil, almost obviates any indication of those of poppy seed oil. This latter yields a white lead paint with very adequate drying properties, which remains quite white, even when exposed to diffused daylight. But white lead ground in poppy seed oil, once dry, is less durable than white lead ground in linseed oil; the latter is thus preferable for particularly durable work, as, for example, in coach-painting. The duration of the mixing process to obtain a fine unctuous paste is very variable. It depends always on the energy with which the mixer works, and also on the total quantity being mixed; finally, it depends also on the surrounding temperature, and of that of the products white lead and oil. It may easily be shown that, in summer, mixing with the same mixer is accomplished more rapidly than in winter. The operation is also more rapid when the mixer is well designed; and brings the constitutive elements of the mixture in perfect contact.

It would be a mistake to believe that the greater the length of time the mixing is prolonged, the better is the product. When the operation is longer than is necessary, the mixture is



certainly more complete, but the material in the end becomes heated, in consequence of the rubbing to which it is submitted, the quality of the oil is altered, and its combination with the salt of lead gives rise to secondary fatty products, the formation of which it is desirable to prevent. This remark is especially applicable in working with linseed oil. Too prolonged mixing ends in a paste with a tendency to string. In the white lead grinding trade, the work of the mixer is regulated so that it uniformly feeds the grinding, which is the succeeding operation, and it may be said, in a general way, that a good mixer ought to have accomplished its work in an hour at the most.

It is almost impossible to specify exactly the moment when the mixing is terminated, owing to the various causes given above, which influence this operation, but, with a little practice, it is easily seized. It can easily be ascertained when the white lead is well mixed, when it exhibits a pasty homogeneous mass, without any dry particles or any free oil, and without any lumps. At this point the blades of the mixer move freely in the paste, and leave therein a sort of track which causes the surface to resemble a series of drawn-out skeins of wool, without, however, exhibiting any viscosity which would indicate a stringy white lead.

2. *Grinding* is the operation which immediately follows mixing. Its object is to finish and to perfect the work of the mixer. Grinding is done in roller mills, sets of apparatus which consist of three parallel cylinders or rolls in juxtaposition, with horizontal axes resting on a frame or foundation. The shaft of the central roll rests, by its two extremities, in fixed bearings, whilst the bearings which support the shafts of the two extreme rolls are movable and can approach or recede from the middle roll, this displacement having, however, but a very feeble amplitude. This opening and closing movement is imparted by very varied arrangements, but which all tend to maintain the parallelism of the rolls as perfect as possible.

It is generally the middle roll which is driven by the motor, and it transmits the motion to the other cylinders by a system of cog-wheels, the diameter of which are calculated so that the central roll makes three revolutions, the back roll only one revolution, and the front roll makes five. Above the two rolls—middle and back—a hopper is fixed, into which the paste, coming from the mixer, is fed; this hopper, the longitudinal axis of which is placed in the line of separation of the two rolls in question, bears in its interior, on the sides perpendicular to the axes of the rolls, rounded pieces of wood exactly embracing the rolls, and ending in sharp points capable of penetrating slightly into the space (always very minute) which separates these two rolls. These pieces of wood, which are often termed *pointes de cœur* (centre points), are regulated by an adjusting screw, which enables them to rise or fall more or less according to the distance between the rolls. Their effect is to prevent the paste from spreading over the ends of the rolls, and thus to be projected beyond them. The paste, falling between the two rolls, is, owing to the difference in their speed of revolution, not only compressed but still further crushed, which in augmenting the fineness of the paste gives the desired result. In virtue of its greater speed, it is the middle roll which charges itself with the greatest amount of substance, which it afterwards delivers to the front roll, the latter, revolving at the greatest speed, rapidly frees the middle roll from the paste with which it is covered. Again, between the two last rolls the difference in their speed of revolution produces simultaneous crushing and compression which finishes the work of the two first rolls. Finally, in front of each set of rolls is the blade of a knife, which scrapes the substance, deposited on this front roll, and allows it to fall into a wooden tub, from which it is taken finished ready for filling into packages.

Ever since its invention, the roller mill has retained this principle of its arrangement, but it has undergone numerous

improvements. The opening out or closing up of the two movable rolls (the front and back rolls) was accomplished, first of all, by means of two adjusting screws, worked by hand wheels acting on the movable bearings, at the end of each spindle. This arrangement had the disadvantage of requiring the workman to perform quite an identical manoeuvre on each of these screws so as to bring about exact parallelism between the two rolls. Later on, this double screwing was replaced in a certain fashion by one only, and for that the bearings of the two extremities of the same shaft are driven by a single axis by means of eccentrics or endless screws. By working on the spindle by a hand wheel, the two bearings are made to recede or advance to identically the same extent. Finally, the use of plummer blocks to support the ends of the spindle of the rolls gives very good results in securing parallelism between the rolls, an essential condition to good working.

In the beginning the rolls were made of cast-iron, but the hardness of this substance was soon recognised as insufficient to produce good grinding, and one of the great advances made in the improvement of this machine was the substitution of granite for cast-iron. At the present day, chiefly in the north of France, manufacturers are going back to cast-iron rolls. But they then use cast-iron which has been hardened specially for the purpose, which in reality is in no way inferior to granite from the point of view of this special property.

As granite rolls can only be made straight from one end to another, it follows that the hopper or feed guards can never be fixed completely tight on the two rolls which it covers, and in spite of the wooden centre piece, the paste escapes and shoots out all along the line of contact, falls outside the rolls, is not ground, and it is necessary to collect it underneath the rolls so as to pass it through them once more.

With cast-iron rolls, made from a pattern, constructed as desired, an abutment can be adjusted to their extremities,

against which the *pointe de cœur* rubs, and thus secures complete tightness to the hopper. Finally, as even granite rolls wear by this continual friction of the paste against them, they must be redressed from time to time. Now the dressing or turning of granite rolls is much more difficult to do than that of cast-iron rolls, and can only be done by means of special corundum mills.

One point is very much discussed in the trade, that is, whether it is preferable to have perfectly smooth uniform rolls, or rolls presenting a slightly granular surface. In Germany they prefer the former; the rolls there are consequently made of perfectly polished porphyry. In France the white lead manufacturers who prefer cast-iron rolls also insist that they be highly polished. This condition of the rolls, producing, according to the manufacturers who adopt it, a grinding, which is perforce very energetic, secures the greatest fineness in the paste, since it is obliged to force a passage between two surfaces which only leave between them an almost mathematical line. Those in favour of granite rolls claim for this material, in addition to the advantage of its hardness, that which it exhibits of presenting surfaces formed, so to speak, of an infinite number of alveoles, very shallow, it is true, but the edges of which are very sharp, and thus divide the material still further, which is, in fact, a form of grinding.

As far as the author is concerned, having used rolls on both principles, he is of opinion that both are equally good, provided, however, that the differences in the revolutions of the rolls be judiciously applied in each case. With granular rolls, such as those made of granite, the difference in speed of the rotation of each of the rolls need not be higher than those indicated above, and the author has many times found that the particles of paste undergo a real tearing, as well as compression. With highly polished rolls these speeds of revolution ought to exhibit a greater ratio in proportion as the substance of which

the roll is composed is more highly polished, consequently this ratio ought to be greater for porphyry than for cast-iron, and therefore greater for the latter than for granite. In that case, in fact, if there be no tearing asunder of the particles of the paste, there is compression, a rubbing-up, for which it is indispensable to allow a sufficiently long time to obtain good work.

As to the tightening of the rolls, the one against the other, this depends on the degree of fineness which it is desired to obtain, the latter being so much the greater as the tightening up is stronger. It must not be exaggerated however, and it should be done in a very gradual manner, so as not to block the rolls, it being well understood that the more the rolls are tightened up, the less is the output of the machine.

The white lead issuing from the rolls is finished, and ready to be delivered to the trade. It must be mentioned, however, that it is often passed through the rolls several times in succession, so as to impart great fineness to it. However, especially in grinding in linseed oil and old tanked oil, it must not be passed through the rolls more than twice, otherwise the white lead paint is liable to be stringy.

Stiff white lead paint, made as just indicated, is delivered in casks, which are filled either directly as the material flows from the rolls, or by lifting it, by the aid of shovels, from the wooden tubs, into which it has fallen as it came from the rolls. When the white lead is intended for immediate consumption, or not exceeding about a month from the time when it was prepared, it is packed in tight beechwood casks; these latter being adapted for 50, 100, and 200 kilogrammes, in round figures, say, in 1 cwt., 2 cwt., and 4 cwt. casks. When, on the other hand, stiff white lead paint in oil is intended to be used, only after the expiry of a long time from its manufacture, it is packed in tinned iron cylinders, perfectly closed, and the lid of which is soldered on. These cylinders (or "silos," as the author also terms them,

which are actually "tin" cans) are in turn packed in casks, which then only serve to protect the metallic package, are somewhat roughly made, and need not be tight.

Finally, when the white lead is intended for exportation—and France exports a large quantity—it is well to fit the tin can with a mouth, placed in one of its bottoms and closed by a cork. This cork is fixed opposite a hole, placed in the bottom of the wooden case, a hole which may likewise be closed by a cork. This arrangement enables the Customs to inspect the goods without having to spoil the package.

Stiff white lead paint, packed in wooden casks, is preserved therein for rather a long time, especially if these casks have already been used for the same purpose, because they are then coated inside with a skin or pellicle of dry white lead which effectually protects the matter contained therein. In new casks stiff white lead paint in oil has a tendency to dry against the sides, the sides of the casks absorbing a portion of the oil contained in the paint. Left in contact with the air, stiff white lead paint in bulk, whether in the cask, or in any other vessel, is rapidly covered by a dry skin, which must be removed and rejected to get at the paint beneath. But this inconvenience and loss may be obviated if care be taken to cover the surface of the pasty mass with a thin layer of clean water. By this means, stiff white lead may be preserved for practically an indefinite period. However, white lead thus preserved, or enclosed in hermetically closed vessels (soldered tin cans), may become stringy after a certain time, which is expressed by saying in trade language that the white lead is *poissante* (which possibly corresponds with the English term "tacky").

#### GRINDING IN OIL OF MOIST WHITE LEAD.

One of the most important steps in advance in the progressive improvements brought to bear in the grinding of white lead

in oil was to perform this operation by bringing directly to the mixer (*i.e.* to the pug mill) the aqueous paste of white lead issuing from the flatstone mills, and mixing it in the pug mill, with the necessary quantity of oil. After a certain time, the oil combines with the white lead and forms a greasy paste, above which there floats in a more or less thick layer all the water contained in the product issuing from the mills.

No one agrees very well as to who was the inventor of this process. Some attribute it to Theodore Lefevre of Lille, others to Expert-Besançon of Paris. All that the author can say on the subject is that the principals of these two firms applied the process almost simultaneously and with equal success.

One observation must be made in regard to this process. All oils do not lend themselves with the same readiness to this elimination of water, and it is poppy seed oil with which this phenomenon is produced most rapidly; and it is said in the trade that poppy seed oil is the oil which *chases*, *i.e.* expels the water the best. It accomplishes this operation, in fact, in half an hour, on an average it may take a little longer in winter than in summer. It depends also on the chemical composition and the regular density of the hydrocarbonate of lead produced by the Dutch process.

The great advantage of this method will be understood, first, from an economical point of view, since it suppresses drying, grinding to powder, sifting of the white lead; secondly, from the point of view of the hygiene of the workmen, who are never exposed to white lead dust. Therefore all the white lead factories make the greater portion of their stiff white lead paint in this way.

The water, floating on the stiff paste of white lead in oil, is eliminated by decantation, and this elimination is complete. Only a few thousandth parts of water can be detected, which is

found imprisoned in sort of pockets which has either escaped grinding, or which has fallen into the finished product. It is well to add that this minimum quantity of water presents no inconvenience in applying the paint.

However long may be the time of mixing, the composition of the stiff white lead in oil remains constant, and is as follows :—

	Per Cent.
White lead brought back to the dry state . . . . .	90
Oil . . . . .	10

It is therefore important that each manufacturer should know exactly the percentage of water in the aqueous white lead paste coming from the mills, so as to be able to add to it the requisite amount of oil in the mixer. Finally, whatever may be the time occupied in mixing, or the temperature at which it is conducted, it is impossible to incorporate, in the stiff white lead, the smallest amount of water expelled by the oil. The stiff paste, as it comes from the mixer, passes to the rolls to be ground, as before, and it is passed through the rolls once, twice, or even three times, according to the degree of fineness which it is desired to obtain. If the water has not been properly decanted, it runs on the rolls, and escapes by the exit from the rolls. If such a paste is passed through a new set of rolls, the presence of this water may render it incapable of taking the stiff paste in oil, on the moistened parts; therefore, in the case just mentioned, it is always necessary, before starting a new set of rolls, to grease them by moistening them with linseed oil, and to turn them against each other in this state for a few minutes. The cylinders, once greased, do not take the water, which rolls along so as to escape by the front roll.

Stiff white lead in oil has rather a variable density, according to the method of making the white lead when the white lead is well made by the Dutch process, its density, when it is in



## THE DIFFERENT VARIETIES OF WHITE LEADS 37

the form of a stiff paste in oil, should be 4, or very near that figure. Moreover, the most dense pastes are generally the most appreciated and, it may be said, the best. As the stiff white lead in oil issues from the rolls, it is packed as described above.

## CHAPTER III.

### OTHER PROCESSES OF MANUFACTURING WHITE LEAD.

IN this chapter, only the different processes of manufacturing white lead, properly so called, will be examined, without reverting either to its grinding to obtain any desired degree of tenuity, or to its grinding in oil. These operations are identically the same as those described for the Dutch process.

It will be understood from what has been said that this process is somewhat empirical, and that it was bound to occur to the minds of chemists to replace it by a rational method based on science. It is to Thénard, in 1801, that the first scientific method of preparing white lead was due—a method more generally known under the name of the Clichy process, which, towards 1830, was more often still called the French process.

#### THE FRENCH, OR CLICHY PROCESS.

It rests on the following chemical reaction:—A current of carbonic acid gas traversing a solution of basic acetate of lead precipitates carbonate of lead and regenerates the normal acetate which can dissolve fresh oxide of lead to form the basic acetate, which is in its turn treated with gaseous carbonic acid. The reaction can thus be rendered continuous. It is always the same acetic acid which figures in the reaction, with the exception of inevitable loss, which a well-constructed apparatus is capable of rendering almost negligible.

In the beginning the Clichy process was wrought thus. In a wooden vat, tarred so as to prevent the disintegration of the wood, litharge was dissolved in acetic acid. An agitator was fitted to the vat to keep the particles of oxide of lead in contact with the acid liquid, and thus assist solution and the formation of basic acetate. When this solution marked  $17^{\circ}$  to  $18^{\circ}$  B., the agitator was stopped and the liquid allowed to settle. The clear liquid was then run into a copper vat, where it clarified completely. When clarification was complete the liquid was sent into the decomposition vat, which was very long and shallow, with a width about half its length, say, 6 metres long by 3 metres wide by 0.9 metre deep (say, 20 feet  $\times$  10 feet  $\times$  3 feet). This decomposition vessel was closed by a lid traversed by numerous copper tubes (800 for above dimensions) which branched off from one or several main conduits and dipped about 0.3 metre (say, 10 inches) into the decomposition vat. It is through these tubes that the carbonic acid—produced in a special furnace by calcining limestone or burning coke—by which the precipitation of the basic acetate of lead is effected, arrives. The carbonic acid thus produced, after cooling and washing, is propelled into the main pipes, and thence into the small tubes. Generally the carbonic acid was aspirated from the furnace which produced it by an Archimedean screw placed in a reservoir of water. The gas was thus both washed and cooled. Thence it was propelled into the main pipes, and thence again into the small tubes, from which it was projected into the solution of basic acetate of lead, where it produced a precipitate of white lead.

Precipitation was complete in twelve hours, and whilst the clear liquid, which should mark  $12^{\circ}$  B., was sent to the tar-coated wooden vat, where it was brought in contact with litharge, the precipitate in the form of paste was sent into a special vat, where it was washed by decantation. This washing terminated, the white lead itself was finished, and the advantage secured by

this method was a sufficiently attenuated product which had no further need to pass through the mills, and the benefit of being able to always use the same acetic acid.

If it was desired to obtain dry white lead, the paste was placed in a stove, as in the Dutch process ; if it was desired to make stiff white lead in oil, it was only necessary to send the paste to the mixer, then to the rolls, and it behaved as indicated above.

Notwithstanding the indisputable logic of the rationale of this process, the white lead produced by it exhibits properties somewhat different from the Dutch process white lead. Thus, for instance, in order to transform it into stiff white lead paint in oil, it absorbs 13 to 14 per cent. of its dry weight of linseed oil, which diminishes both its consistency and density, two properties much sought after by the painter. Finally, it has less covering power than Dutch process white lead, and that is rather remarkable, as it is opposed to that which occurs with all pulverulent products mixed with oil for paint purposes.

It, in fact, may be taken for granted that the more finely pulverised such a substance is, the greater is its covering power. When such a substance is in the amorphous state, it has more covering power than when pulverised ever so fine by grinding. One of the most striking examples of this nature is that of sulphate of baryta. When the latter is obtained by pulverisation of the natural rock (barytes), even when pushed to an extreme degree of fineness, it, so to speak, does not possess covering power. But precipitated sulphate of baryta, if not to be compared with white lead, has yet a certain amount of covering power. Indeed, it is much used in this condition for mixing with special colours, to attenuate their shade so as to produce different tones of the same colour.

\* It would seem, therefore, at first sight, that white lead made by the Clichy process ought, as compared with the Dutch process white lead, to present the same advantage of superior

covering power, since it is an amorphous powder, and in a much finer state of division. However, such is not at all the case, and a very long experience has always assigned to white lead by precipitation a covering power notably inferior to that of Dutch process white lead, in spite of the many very judicious improvements brought to bear on the manufacture of the former.

Amongst these there may be pointed out that which consisted in only using very pure carbonic acid, which has caused resource to be made, for its production, to the most improved forms of limekilns. Later on, Ozouf again secured a more pure carbonic acid by drawing it from the combustion of coal, and, after submitting it to several washings, causing it to be absorbed by a solution of carbonate of soda marking 9° Baumé when cold. Bicarbonate of soda was thus formed, which was decomposed by heat. The carbonic acid which he collected, freed from extraneous gases, was stored in a gasometer, whence it was taken gradually for precipitation purposes.<sup>1</sup>

Pallu, who occupied himself much with the preparation of white lead by precipitation, and who brought numerous improvements to bear on this industry, remarked that when white lead is precipitated as described above, the first portions of the precipitate yield a superior product to that obtained towards the end of the operation. He therefore concluded, not without reason, that the precipitation ought always to be made in a highly concentrated lead solution. He therefore restored the oxide of lead to the liquid in proportion as it was precipitated, in such a way that the carbonic acid was never in presence of a weak solution of basic acetate.

On the other hand, Ozouf attained the same result by passing the carbonic acid into a vessel where the solution of

<sup>1</sup> See Bersch's *Mineral and Lake Pigments* (Scott, Greenwood & Son), pp. 105-110, for fully illustrated description.

basic acetate was distributed in the form of a regular shower of rain.

But, as already mentioned, these improvements never enabled a white lead to be produced, the covering power of which was equal to that made by the Dutch process. No painter would take it, without a notable reduction in price; and, finally, all the French factories which made white lead by precipitation have disappeared, or have reverted to the Dutch process.

#### HOT CHAMBER PROCESS.

This process, as already described at the beginning of this volume, is a variation of the Dutch process, in the sense that it applies artificial means to obtain the same effects as those got by the stack. The stack is replaced by a vast chamber, in wood or masonry, in which sheets of lead are suspended on laths or batons. The leaden sheets are generally very thin; but their surface varies somewhat with the factory. Some use sheets which do not exceed a kilogramme (2·2 lbs.), whilst others impart such dimensions to these that they weigh 10 and even 20 kilogrammes (22 and 44 lbs.); they are then folded in several parts, for here also care must be taken to impart to the metal the largest surface for attack possible.

A chamber being charged to its full capacity, it is closed hermetically, and hot carbonic acid distributed by different pipes, so as to come in contact with all the plates, is injected; with this current, and entrained by it, likewise comes the acetic acid vapour, and steam from a boiler. All the active elements are thus combined, the functions of which have already been described in dealing with the stack process.

The metallic lead is converted into white lead in two or three weeks, and such conversion is almost complete, for from a chamber charged with 10 tons of metallic lead, only 200 to 300 kilogrammes (say, 4 to 6 cwt.) of unattacked blue (metallic)

lead is drawn out, which, remelted, is again used. In order to discharge a chamber, at the close of an operation, care is taken to inject a very strong current of steam, so as to well moisten the material, and lay dust when discharging.

The operations which follow this conversion are identical with those already described.

Even though it imitates in every point what happens in the stack of the Dutch process, this method still gives a different white lead. It generally exhibits a frothy (dendritic?) aspect, with softer scales than those produced by the Dutch process, and yields, in the end, whether in the form of a dry powder, or in the form of stiff paste in oil, a less compact and dense product than that produced by the Dutch process. These are two characteristics, regarded as defects by the paint trade, which explain why the product thus obtained is less appreciated and is sold at a lower price.

#### KREMS PROCESS.

This process is adopted in a very general way in Austria, and yields a product of repute. It may be said of it that it is the reproduction by artificial means of the Dutch process, to which it approaches more than the hot chamber process, although using partially the same means.

In the Krems process the stack is replaced by a larger or smaller chamber, artificial heat is substituted for that of farm-yard dung. As to the production of carbonic acid, it is obtained by the fermentation of the marc (skins, etc.) of grapes, or of other fruits.

In actual practice the operation is conducted as follows:—Into a chamber of variable dimensions, according to the factory, there are introduced wooden cases, tarred inside, to which the following dimensions are generally given: length 1 to 1·5 metres, width 35 to 40 centimetres, depth 30 to 35 centimetres. The bottom of each case is lined with a layer of grape skins,

or of skins of different fruits, mixed with acetic acid. Above this layer thin sheets of lead slightly folded are suspended on laths; they ought to be fixed on the laths in such a way that their edges do not touch each other nor the sides of the case.

The cases thus prepared are placed to the number of 90, 100, or even 150, in the closed chambers, the temperature of which is progressively raised as follows:—The first week the temperature is kept at 25° C. (77° F.), the second week it is brought to 38° C. (100·4° F.), the third week to 45° (C. 113° F.), and the fourth week it is brought to 50° C. (122 F.). Then it is left to cool slowly, and the operation is finished at the end of six weeks.

The reaction which occurs will be understood at once. The heat to which the chamber is subjected, by whatever system of heating, causes the acetic acid to be vaporised, at the same time as the fermentation of the fruit mares generates carbonic acid. It is, as will be seen, a variation of the Dutch process, a happy variation, it may be said, as the white lead so obtained is particularly beautiful as regards whiteness. This property has for a long time been ascribed to the exceptional purity of the metallic lead used at Krems, and to the fact that all the Austrian white lead manufacturers endeavour to obtain this lead, which amongst other properties is absolutely exempt from iron. The author rather believes that the very special whiteness of this white lead arises from the fact that the marc (grape skins, etc.) used contains no trace of sulphur, and consequently, during the progress of its fermentation, no sulphuretted hydrogen is evolved. In farmyard dung, and spent tan, on the other hand, whatever care may be exercised in the choice of raw materials, it is impossible to avoid the formation of very small but perfectly appreciable quantities of sulphuretted hydrogen. If, in addition, the lead contain a little iron, the sulphide, which then forms, is not absolutely



black, but verges a little towards maroon, which imparts a rose tint to the white lead. This tone is not perceptible, it is true, unless placed in contrast with an absolutely pure white, such as starch powder. White lead, by the Krems process, contrasted in the same way, retains a perfectly pure white colour.

In order to discharge the cases, the sheets of lead covered with white lead are drenched, and the remainder of the operations are identical with those described under the Dutch process. Mention may, however, be made in passing of a peculiar feature of the Krems process of white lead manufacture. Before sending the white lead detached from the sheets, to undergo the succeeding operations already described, manufacturers select the whitest and the most beautiful scales, which they reduce to powder by processes already described, and thus produce therefrom a special quality, *silver white*. Indeed, the best silver white comes to us from this source; it is often imitated by white lead obtained by precipitation.

#### ENGLISH PROCESS.

This will only be mentioned as a matter of history, because it appears to be abandoned even in England, where it was invented. Moreover, the numerous attempts made in France to work this process have almost all failed, the method in question would appear, therefore, to be condemned.

The English process, which has sometimes been called the Quick Dutch process, is founded on the simultaneous action of acetic acid, or acetate of lead, on litharge and carbonic acid.

In actual practice, very dilute acetic acid was mixed with litharge so as to form a rather thick paste, which was spread on leaden plates. These being arranged in a closed chamber, a current of pure, well-washed carbonic acid gas was passed into it. The absorption of the gas was facilitated by stirring the pasty mass from time to time by scrapers. A fresh amount of

litharge was added in two or three different applications during the course of the manufacture. The mass was gradually converted into white lead, and the operation finished in six weeks.

The white lead produced by the "English" process was of inferior quality, because it was less dense than white lead by the Dutch process, and easily absorbed 14 to 17 per cent. of oil, during its conversion into stiff white lead paint. Some manufacturers nevertheless, by prolonging the time occupied in mixing this white lead with oil, by using mixers driven particularly energetically, were enabled to reduce the percentage of oil and to bring it down to 13 to 14 per cent., but then the paste obtained was more compact, which for a long time has caused it to be said that white lead by the "English" process was very hard. The painters who used it found themselves obliged to increase the liquid portion, oil and spirits of turpentine, introduced into the paint, which caused it to cover less and in many cases to cost more than white lead prepared by the Dutch process.

## CHAPTER IV.

### WHITE LEAD SUBSTITUTES.

#### SOPHISTICATION OF WHITE LEAD—ANALYSIS OF WHITE LEAD.

ALL the products which have been proposed as substitutes for white lead will not be examined here. It may be said they are legion, especially of late years, during the course of which a very vigorous campaign has been pursued with the object of suppressing the use of white lead, which is not without presenting real danger in its application. There are, however, two which merit special mention, because they constitute quite special products. These are lithopone and zinc sulphide.

#### LITHOPONE

Lithopone is produced by double decomposition of barium sulphide and zinc sulphate, which give a precipitate consisting of a mixture of barium sulphate and zinc sulphide. These two products are very white; the precipitate, washed, dried, often calcined, then thrown into cold water, is reduced to a fine powder, then mixed with oil to a pasty consistency.

The stiff paint which lithopone affords with oil has the appearance of a very fine white lead, and would lead one to believe that in it they had actually found the true substitute for white lead. Experience and use has, however, shown that the hypothesis was not well founded. Lithopone, in fact, has much less covering power than white lead, which is easily

explained by the enormous quantity of barium sulphate which it contains, for the chemical formula of the reaction indicated above specifies by weight the following percentage:—67 per cent. of sulphate of baryta and 33 of zinc sulphide. As to zinc sulphide, it seems to combine in a way with the oil, and consequently to approach thereby white lead, which forms—in a chemical sense—with the oil a real lead compound. But the presence of zinc sulphide in lithopone is not always without inconvenience. Thus, in the painting of certain metals—iron, for example,—zinc sulphide tends to abandon its sulphur to the iron to form a sulphide of iron, a fact which painters often express by saying *lithopone rusts iron*. Finally, it must be mentioned that zinc sulphide, in virtue of its sulphur, tends strongly to combine with the oil, but this combination, which greatly resembles a vulcanisation of the oil, is liable to decompose it, and it is to this cause that the author attributes the poor permanency and durability of painting done with lithopone.

Amongst the other defects of this product which must be pointed out is the irregularity which it presents as regards quality. This irregularity arises from the extreme difficulty which exists of obtaining commercially barium sulphide of constant composition. Another great drawback of painting done with lithopone, which is likewise urged against it, is that it eventually exhibits very diverse shade, varying from white to greyish white, often passing to rose, to violet, etc. Researches made to discover the cause of these abnormal colorations have attributed them to the presence of different metals, contained in the zinc sulphate.

To sum up, without absolutely condemning lithopone, which may find its place in a certain class of painting, the author, nevertheless, thinks that its use will never become general, like that of white lead, even though numerous actual improvements have been realised in its manufacture. Of these there may be pointed out those the object of which is to purify the zinc

sulphate, efficiently and practically, so as to free it completely from the impurities which produce the above-mentioned colorations. This product, very widely used in Germany, is manufactured in France by a few special factories, who (the author must do them this justice) set themselves, as much by improved plant as by special care brought to bear on the manufacture, to produce a pure product.

Lithopone generally covers rather badly; it is almost impossible to apply it on iron for the reason already given. Its use for painting wood, new wood especially, gives bad enough results; on the other hand, the author has seen it applied, not without success, as a surface coating on plaster, intended to be covered with 2 or 3 coats of ordinary paint. Its principal advantage is its comparative cheapness in so far that lithopone stiff paint in oil is currently sold 10 francs, at least, per 100 kilogrammes (say, 4 shillings per cwt.) below the price of white lead.

As, according to the degree of acidity of the solution of zinc used to make the double decomposition, it is easy to obtain lithopone with a valuable percentage of barium sulphate, but never below 67 per cent., manufacturers sell this product, according to the variable percentage of zinc sulphide and barium sulphate. They thus sell lithopone as  $\frac{2}{3}$  or  $\frac{3}{10}$ , which signifies 33 of zinc sulphide and 67 of precipitated barium sulphate, or 30 of the first and 70 of the second, for qualities are made containing as much as 80 per cent. of barium sulphate for 20 per cent. of zinc sulphide.

#### ZINC SULPHIDE.

Zinc sulphide as a stiff oil paint has for some time been greatly recommended as a substitute for white lead. This body gives, it is true, with oil a paste of a very pretty appearance, perfectly homogeneous, and which dries well enough. But leaving its whiteness, very pure and perfectly inalterable, out of account, it is difficult to see the technical reasons which can

justify the use of this product in painting. It presents the defects, inherent to zinc sulphide, which have been pointed out in connection with the zinc sulphide present in lithopone. If the preparation of zinc sulphide as a stiff paint does not cost more than the preparation of white lead stiff paint, the industrial manufacture alone of the zinc sulphide, as a dry powder, still produces a relatively high-priced product, and finally of a stiff paste in oil costing 80 to 100 francs the 100 kilogrammes (say, £1, 12s. to £2 the cwt.).

#### VARIOUS WHITES.

It must be pointed out, as a matter of history, that inventors of all times have thought they have discovered a substitute for white lead, because they have obtained a white powder, easily miscible with oil, to form a paste presenting all the appearance of that made with white lead. Thus the most diverse products are to be seen, made up of mixtures of bodies, neither of which have any affinity for oil, and which form, as the basis of paint, products the quality of which is not inferior but absolutely negative.

#### SOPHISTICATION OF WHITE LEAD.

Like every other product which the consumer greatly endeavours to obtain, white lead, whether dry, or as a stiff paint in oil, undergoes numerous sophistications with the view of lowering its price and increasing the profit on it to the seller. Let it be at once said that sophisticated white leads are always sold (in France) without a mark (brand), and whoever wishes to be assured of getting this product absolutely pure has only to specify that it should bear the mark (brand) of one of the French manufacturers (corroders) of white lead. These have, in fact, unanimously agreed to the principle of only selling pure white lead. Therefore, the more or less sophisticated product is only to be got from retailers, or the less conscientious grinders.

To carry out the sophistication, the most diverse products are used, and the one most generally employed is certainly finely pulverised natural barium sulphate (barytes), or sometimes the precipitated form of the same body; next come lead sulphate, sulphate of lime (terra alba), carbonate of lime (Paris white), carbonate of baryta (witherite), china clay (kaolin), etc. If the most widely used agent of sophistication be barium sulphate, it is on account of its great density, its cheapness, and also because it is the product which, after zinc white, diminishes the covering power of white lead to the least extent.

## ANALYSIS OF WHITE LEAD.

Before giving the complete analysis of white lead, the following is a rapid method of testing the product when it is suspected of containing barium sulphate, which is the most frequent adulterant. Ten grammes of the perfectly dry white lead are calcined in a porcelain crucible. The pure white lead loses on an average 14·5 per cent. of its weight, a mixture of—

80 per cent. white lead and	}	loses 13 per cent.
20 per cent. barytes . . .		
50 per cent. white lead and	}	loses 10 per cent.
50 per cent. barytes . . .		
66 per cent. white lead and	}	loses 6·5 to 7 per cent.
34 per cent. barytes . . .		
34 per cent. white lead and	}	loses 3·4 to 5 per cent.
66 per cent. barytes . . .		

If the white lead to be tested as above be in the form of a stiff paste in oil, a sample is taken, which is well washed by carbon disulphide, benzine, or carbon tetra-chloride, and the operation described above is performed on the perfectly dry product so obtained.

In order to make the complete analysis of a white lead, the sample taken is brought to the state of a dry powder if the product is ground in oil, then treated by dilute hydrochloric

acid, which dissolves all the carbonates, except that of baryta. If complete solution is effected there is a probability that the product is pure, but it is only a probability, and complete analysis necessitates that the operation should be conducted as follows:—

A.—Solution in hydrochloric acid is complete. It is precipitated by sulphuretted hydrogen filtered, the filtrate neutralised by ammonia, and ammonium sulphide added. Two cases present themselves:—(1) No precipitate. Add ammonium carbonate to the liquid: if a precipitate be formed, the product contains carbonate of lime or baryta; if no precipitate, the sample is pure white lead. (2) There is a more or less abundant precipitate: it is treated by dilute acetic acid, and collected on a filter, if it dissolves the white lead contains phosphate of lime. If only little or no solution occur, and the precipitate is soluble in hydrochloric acid with disengagement of sulphuretted hydrogen, it is due to oxide of zinc contained in the white lead.

Solution A leaves a residue on the filter, it is filtered, washed well where a portion is drenched with sulphuretted hydrogen. If the residue be coloured black, it is lead sulphate.

If there be no coloration, a portion of the dry residue is calcined with charcoal, and the mass is treated, after calcination, with sulphuric acid. Two cases may present themselves:—(1) Solution with evolution of sulphuretted hydrogen. The filtered liquid to which a solution of sulphate of lime has been added (*a*) gives a precipitate, sulphate of baryta is present. (*b*) No precipitate, sulphate of lime is present. (2) There is no disengagement of sulphuretted hydrogen, the white lead contains a silicate.



## CHAPTER V.

### WHITE LEAD PAINTS—THEIR MERITS AND DEFECTS.

**I**T may be said that white lead gives a typical paint. Now it must be understood that a typical paint is one which exhibits the following characteristics :—The capability of being spread in a very thin elastic coat, which coat ought to dry very rapidly without the addition of driers, it being taken for granted that a good paint ought to dry in two days. All these conditions are fulfilled to a nicety by white lead, and constitute its own peculiar properties, which up to the present day at least no other product has been able to attain completely.

Finally, white lead possesses a very pretty white colour, which is also a distinctive property, because mixed with staining colours, so as to produce special tints and hues, it does not radically alter (*denature*) these pigments, it can only diminish their intensity (or reduce their depth of colour), more or less, a property which is taken advantage of to impart to the same pigment a whole gamut or scale of different graduated tones.

The author does not deem it necessary, however, to insist too much on the whiteness of white lead; other products, zinc oxide, for example, possess this property to an equal extent at least. The author rather insists upon this point, as, in the minds of many practical men in the trade, nothing equals the whiteness of white lead, which causes them to reject unmercifully any substitute for white lead, even if it exhibits all the other qualities thereof, but has not exactly the same

whiteness. The author believes that this is a mere question of use and wont on their part, and they being accustomed to a certain tone of white, that of white lead, all other tones no longer appear to them a perfect white.

The prolonged personal researches of the author on this question justify him in thinking that, as regards white, there are different tones in existence, just as there is in the case of other colours, and in the absence of a well-defined coloration, it is difficult, if not impossible, to give an opinion by the unaided eye, on the more or less perfect whiteness of any such product when compared with another similar one.

Here, moreover, is an effect which has often been remarked. Taking different white products ground in oil, when they are viewed separately, they appear absolutely white; but, when brought near one another, this whiteness differs in the case of each of them. Indeed, it is a fact well known to all white lead manufacturers, that Dutch process white lead ground in oil has a very characteristic rose tone compared with zinc white in oil. Is that to say that the white lead is not white? No, certainly not; but it has a different tone from that of zinc oxide. Again, take two oxides of zinc, equally pure from a chemical point of view, but obtained, the first by distillation of the metal, and the second by direct calcination of the ore, these two oxides, ground in oil, exhibit between each other a difference in whiteness. The white of the first will be slightly green, that of the second slightly ivory, and each of them taken separately would appear to be perfectly white. This last example affords an explanation of the difference in tone which the same pigment may possess, because it is due here to a difference in the molecular condition of the same body. In fact, zinc oxide, made by distilling the metal, presents itself in the form of small flakes with more or less barbed edges, mixed with a small number of almost spherical grains; the oxide produced by calcining the ore consists, on the contrary, of

a mass of almost spherical grains, mixed with a very small number of flakes. It therefore appears certain that the play of light through these two masses of corpuscles, of different shape, is itself different, and gives rise to products of different tones. Bodies of different composition exist, *a fortiori*, in different molecular states, hence, in the opinion of the author, the cause of these slight variations in whiteness to which it is not necessary to attach a primordial importance, as one is too much inclined to do.

It is elsewhere than in its whiteness, that it is necessary to seek for the characteristic properties of white lead, and Stas is the first who has explained these scientifically in his theory of white lead painting in oil which begins with this sentence, which all those who seek after substitutes for white lead ought to have engraved in their minds. "It is wrongly imagined that white lead paint is a mixture of a white powder with oil, and that, consequently, it is possible to replace white lead by any other white powder mixed with oil, with oil rendered siccative if need be."

It is the ignorance or the forgetfulness of this highly sound principle which has led to the production of a whole host of products, intended, in the minds of the makers, to replace white lead, but which do not possess a single one of its properties. But, still following Stas in his theory of white lead painting, this is what he says:—

"So that it may be well understood, we must, first of all, recall the chemical nature of white lead. We know that this substance, prepared by all the practical processes known, is not a carbonate but, in fact, a hydrocarbonate of lead, containing more or less carbonate, and covering so much the better the less hydrate of this metal it contains. The best washed white leads always contain a trace of basic acetate of lead; moreover, many commercial white leads contain the neutral acetate or the dibasic acetate of lead.

"Liebig was the first to show that lead oxide can dissolve in a somewhat large amount of linseed oil without saponifying it.

"Linseed oil thus acquires very drying properties; the secular use of oxide of lead to render that oil more drying more than proves the fact.

"At the ordinary temperature, and especially at a high temperature, linseed oil may likewise dissolve the basic acetates, and even the neutral acetate of lead. The solution of acetate of lead in oil when it comes in contact with air disengages acetic acid at the ordinary temperature.

"The oxide of lead dissolved in oil, whether by digestion with the anhydrous or hydrated oxide, or by contact with acetates of lead, saponifies it after a certain time, because it contains a certain quantity of water; linoleate and margarate of lead are thus produced, which, being soluble in oil, and in very considerable proportion, the linoleate especially, remain in solution.

"Linseed oil, holding in solution either oxide of lead, or linoleate or margarate of lead, in greater or less amount, dries in contact with the air. The oil which contains the dry oxide dries sooner than that containing the linoleate or margarate of lead; but both the one and the other, applied on a surface, form after the oxidation of the oil a plumbous varnish, dry to the touch, transparent or milky, or even white and almost opaque, according to the amount of linoleate or margarate dissolved.

"This varnish exhibits great elasticity, and resists rubbing better than that obtained by dessication in the air of oil, which does not contain lead; it contains linoleate and margarate of lead intact.

"Let us now apply these facts to the preparation of stiff white lead paint in oil. When it comes to the mixing and the subsequent grinding of white lead with oil, a portion of

the hydrate of lead and of the acetate of lead which are contained therein (*i.e.* in the dry white lead) dissolve in the beginning. By allowing the paste to stand by itself out of contact with air, a fresh and larger amount of lead oxide is dissolved. Thus we know that white lead paint, preserved under water or in a closed vessel, ends by becoming tacky. The tackiness of the paste is generally attributed to the rancidity of the oil alone, but we (Stas) have determined that this gluey state is due principally to the formation of a lead soap, which dissolves in the oil.

“When it comes to thinning down the stiff paint in a suitable quantity of oil, to render it fit for use, and when such paint is afterwards applied on any given surface, it dries, owing to the air, and the coating consists essentially of carbonate of lead, containing a little hydrate of lead. These particles of carbonate of lead, a white opaque body, are enveloped, even soldered together, the one to the other, by the margarate of lead which imparts opacity and elasticity, and the linoleate, especially, much impermeability to the coat.

“When the paint is exposed to the causes which in general destroy it most rapidly, such as the direct rays of the sun and moisture, the oil which has become oxidised is consumed; but the destruction thereof is delayed by the impermeability of the lead compound which it contains and which covers it. Under the influence of the rises and falls (changes) of temperature, the paint is less liable to crack, split, and to fall off in scales, owing to the great elasticity which the linoleate and margarate of lead impart to the oxidised oil.

“White lead therefore contains in itself the cause of the drying power which it communicates to the oil. It cedes the oxide of lead to the oil, which produces this effect. This oxide of lead, by gradually saponifying a certain amount of oil, forms a metallic salt, soluble in the oil, which remains dissolved after the oil has dried, and communicates to the

substance which results from this oxidation both elasticity and impermeability.

“White lead therefore owes to the chemical nature of the compounds which it contains the cause of the permanency of the paint into which it enters, but it also owes this permanency to the ratio in which these compounds exist; because, if the nature of white lead be changed either by diminishing or increasing beyond measure the amount of hydrated oxide of lead, or of basic acetate of lead, which it commonly contains, the properties of the paint which it produces are changed at the same time. Thus it is known that the introduction of a large amount of litharge gives a siccative pigment, very hard at first, but very liable to crack by the alternations of temperature, and even to crumble (*fariner*), as artists in oil sometimes notice on their canvas prepared with white lead to which litharge has been added.”

Such is the theory enunciated by Stas, which has the grand merit—if it be not absolutely exact as to the products formed by the mixture of oil and white lead—of remaining perfectly true in its basis or foundation, which may be summed up in the following manner without causing the precise terms of the reactions which occur to intervene:—White lead, like all salts of lead, like metallic lead itself, possesses great affinity for oils in general, and the fixed fatty oils in particular. It tends therefore, in presence of the latter, to form real chemical compounds which are salts of lead, more or less soluble in the linseed oil, afterwards added to impart the desired fluidity to a paint during its application. These salts become modified afterwards by the oxidation itself of the oil, exposed to contact with the air, and give rise to substances possessing the qualities required in good paint, elasticity, and a certain hardness. Granted that there is combination between the elements of the white lead and the oil, and solution of the salts of lead formed in the oil added to the paint, so that the paint can be

applied in an exceedingly thin coat, the thinned paint none the less preserves all the qualities of the said combination.

The only point where the theory of Stas may lend itself to criticism is principally as to the nature of the salts of lead obtained by the combination of oil and white lead. Genuine linseed oil ought not to contain margaric acid, it cannot therefore form margarate of lead with white lead.

Another point, demonstrated long after the researches of Stas, is that linseed oil exposed to the air is transformed by absorption of oxygen into oxylinoleic acid; it appears, therefore, rather probable that the linoleate of lead, of which Stas speaks, ought itself to become transformed by the action of the air into oxylinoleate. But the author reasserts that these are only, so to speak, errors of expression; the very foundation of these phenomena follows well the course indicated by the eminent chemist.

Finally, it may be said that all are agreed at the present day to regard the first chemical combination, in the mixture of oil and white lead, as taking place between the hydrate of lead and the oil, and that the carbonate rests simply enshrouded in this compound to form the opacity of the latter. As to the presence of the basic or neutral acetates of lead which Stas was, in fact, able to find in the white leads of his epoch, which might very well intervene in the general reaction between the white lead and the oil, that is only an exceptional occurrence at the present day, thanks to the improved methods of levigation adopted in all well-conducted white lead works.

To resume, all the good qualities of white lead paint lie in the fact that white lead mixed with oil gives rise to a chemically combined product possessing the special properties required in paint.

Therefore, every time that one tries to find a substitute for white lead, he should first of all use his utmost endeavours to find a body capable of combining with oil, soluble in the

latter, and which is very white, so as not to modify the tint of the pigments used. It is the violation of this law—a purely chemical one—which has caused a whole host of products, known in the paint trade as white lead substitutes, which we have silently passed by, to come to grief. Only lithopone and zinc sulphide have been described, being the only ones capable of reacting chemically with oil, the first owing to the presence of a small quantity of the second. Does the nature of the product which is produced by this reaction render it really utilisable for paint purposes? That still remains to be proven.

As to the defects of white lead, they are of two classes from a pictorial point of view alone. White lead, like all the salts of lead, has the defect of blackening under the influence of sulphuretted emanations, which, in fact, forbids its use in w.c.'s., kitchens, bathrooms. In neighbourhoods with a system of illumination by gas, white lead painting is liable to lose its whiteness, by the action of the traces of sulphuretted hydrogen produced by this style of illumination; it is therefore said that the colorations thus produced have caused the paints to lose their freshness.

The second defect of white lead of a hygienic order is that of being a poisonous product which must only be handled with the greatest of precautions. This subject will be dealt with in the next chapter.

#### WHITE LEAD *ENDUITS* (PUTTY AND FILLING UP).

All which has been said in regard to white lead paint applies to white lead “putty,” which should only be stiff white lead paint in oil, but stiffer than that intended to be used in making liquid paint, and which is spread or laid on by the putty knife.

Pure white lead putty is made from the stiff paint in oil, already described, to which enough white lead is added, in powder, to bring it to the consistency of glaziers' putty. How-



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ever that is not the only standard of consistency used, it, in fact, varies with the job on which it is to be used. The putty or filling is applied generally on very particular work; and on it, when well dried, the coats of paint are applied. The object of it is to give to the parts to be painted a perfectly uniform surface. Therefore, when the surface is not very rough, a putty of comparatively poor consistency may be used, such is the case with fine plaster; in the case of coarse plaster, a putty of somewhat strong consistency is used. So as to reduce the cost of the putty, there is often mixed with the stiff white lead paint a certain amount of finely pulverised and sifted Paris white. The more the putty contains of this last body the poorer it is, but the white lead, nevertheless, causes the Paris white to participate in its own properties, and the putty consisting of half white lead, half Paris white, is still very good for current work. On very particular jobs, as in coach-painting, it is necessary to use pure white lead putty. The white lead putty, or mastic, is plastic, and embraces all the sinuosities and preserves the shape taken. It dries very rapidly. It may be rubbed down with glass paper, or pumice stone, and, so worn down that, throughout all its thickness, the layer, even when very thin, which still remains, presents all the properties of resistance and permanency which are the special characteristics of white lead paint.

## CHAPTER VI.

### TOXICOLOGY OF WHITE LEAD.

#### HYGIENIC MEASURES IN ITS MANUFACTURE AND USE.

WHITE lead, as everyone knows, is distinctly poisonous, and its introduction into the system brings about the grave complaint known under the name of *saturnism* (plumbism, or, in plain English, lead poisoning). This introduction may occur through the alimentary canal, through the lungs, by the mucous membranes, even by the skins of certain individuals, the latter forming, it is true, the exception.

The first symptoms of lead poisoning are characterised by languor, very great muscular feebleness, and insomnia; then there appears a blue line along the gums, which is always accompanied by violent colic, called lead colic. Constipation is obstinate, urination scanty, and the patient has frequent nauseas, followed by bilious vomiting. Having reached this condition, if the *saturnin* continues his work, the above symptoms become acute, ending in encephalopathy, in the paralysis of the extensor muscles, in cachexy, and finally in death.

In the trade, the toxicology of white lead may be divided into two categories: (1) that which affects the workmen in white lead factories; (2) that which affects the users of white lead, the majority of whom are painters and glaziers.

In the first category it may be affirmed that lead poisoning is more rare. It is, indeed, a case of a dangerous substance, it

is true, but in which everyone, from the principal downwards to the last labourer, knows very well the danger, and consequently where active supervision and especially the goodwill of each are able to conjure such a terrible evil as plumbism.

It has been seen that, in everything connected with the manufacture of white lead, there is not a single operation for which the most rigorous methods are not indicated for the purpose of avoiding all danger, and one can, therefore, be assured that they are adopted in all white lead factories, because, apart even from the sentiment of common humanity, the principal is compelled to apply them, it being taken for granted that all white lead, diffused through the atmosphere, constitutes a loss which must be avoided, so as to reduce the cost price as low as possible. There is, however, an obstacle which often opposes itself to the manufacturer anxious for the health of his workmen, and that is the negligence of the latter, to whom it is often very difficult to apply the most elementary means of preserving themselves from the hurtful nature of the product which they handle. Thus it has been mentioned above that each man touching the sheets covered with their scales should have on gloves. Such a method of preservation is very simple, and yet workmen do not adopt it in spite of the recommendations which have been made to them. One cannot, therefore, urge too strongly that an assiduous supervision should, every moment, be exercised over all the staff at whatever spot they may happen to be posted. It is well understood that the same supervision ought to be brought to bear on all the plants destined to evacuate white lead dust, or to collect such in depositing chambers.

Outside the average workmen, who scrupulously follow all the precautions recommended to them, there exist constitutions particularly inclined to lead poisoning. Thus the principal,

who engages a new workman would do well to submit him to the inspection of the factory doctor, and if the latter recognises in him one of these peculiar constitutions he ought to cause him to be excluded from the staff of the factory.

Amongst the antidotes for lead, milk seems to be that which is the most efficacious; white lead manufacturers therefore do well to use it freely. In this way the author has seen, at the factory of M. Expert-Besangon, this use made imperative. In this factory, in a large hall, remote from the manufacturing buildings, three distributions of milk are made, the first at six o'clock in the morning on the entry of the workmen, the second at nine o'clock, and the third at three o'clock. To the nine o'clock dose there is added a teaspoonful of a solution of hyposulphite of soda (150 grammes per litre, *i.e.* 150 grains per 1000 grain measure, or  $1\frac{1}{2}$  lbs. to the gallon).

Amongst the other hygienic measures appertaining to the individual, this same firm has installed a large dressing-room, and wash-stands, where each workman possesses his cupboard with two compartments, the one for working clothes, provided by the firm, the other for his town clothes, which he must put off on entering the factory, not to put them on again until he goes out of it.

The workmen are required, during time for which, moreover, they are paid, to wash very carefully their hands and faces, and to wash out their mouths before quitting the factory. For that purpose they have at their disposal hot water, soap, towels, and sodium sulphide. This product, which precipitates lead as black insoluble sulphide, in fact, warns the workman if the washings which he has performed have well eliminated the lead which he might carry about him.

Installations of shower-baths, and bathrooms, by which twenty-five baths can be given in the same day, complete the installation made to provide for the hygiene of the workmen.

Finally, a doctor inspects each of the workmen at least once a week, keeps a very complete register, as to the state of health of each workman, whom he can follow up, and not hesitate to stop working, if he sees the least sign of poisoning.

These are excellent measures which cannot be recommended too much, and which all white lead manufacturers should energetically impose on all their staff.

The hygienic measures to be taken by the users of white lead, principally painters and glaziers, are very difficult in application, because the workmen in question for the greater part are spread through workshops of greater or less importance, are left to themselves without supervision, their negligence, their heedlessness of the danger, often cause them to neglect the recommendations, nay, even the orders, intended to protect them from a terrible evil.

It seems likely that the most efficacious means of preserving the painter from lead poisoning would be found in the education of the apprentice. The latter should be warned, as soon as he commences to learn the trade, that he has to handle one of the most dangerous of products, and this warning should be renewed on every occasion. It is necessary also that he be interdicted from smoking, especially cigarettes, the paper of which he impregnates with white lead. It is necessary also to accustom him never to quit the workshop without washing his hands and face, and rinsing his mouth. It is also necessary to train him to keep all his tools, brushes, knives, truck handles, etc., in a state of fastidious cleanliness. Finally, it must be stated that, as in the case of white lead factory workers, there are painters to whom on account of their constitution, the trade of painter should be forbidden.

Amongst painters, there is a specialist who is more liable to lead poisoning, and that is the *enduiseur*, or filler-up. But as regards him, also, it is a case of training. The *enduiseur*, in fact, has the very bad habit of holding the white lead which

he has to apply with the knife, in his hand. Now it seems that if from the beginning of his apprenticeship this workman were trained to work with gloves, or to hold his putty on a palette, he would, once accustomed to this method of precaution, have the same skill as the present *enduisseur* (filler-up).

Finally, another very dangerous operation may be pointed out. It consists in sand-papering or pumicing coats of stiff white lead paint. The dust which is produced during this operation, being easily absorbed by the workmen either by the alimentary canal, or by the lungs. The best and most simple means consists in never doing this class of work without keeping the paint or filling-up so treated drenched with water. The dust in question is then immersed in water, as soon as produced, and is not diffused into the atmosphere.

## CHAPTER VII.

### ZINC WHITE—ITS PREPARATION.

THE idea of substituting zinc oxide or zinc white for white lead, in painting, is not new; it goes back to 1780. Some attribute it to Courtois, a demonstrator of the laboratory of the Academy of Dijon; others to Guyton de Morveau, magistrate at the Court of Dijon, of whom Courtois would have been the collaborator. Whatever may be the real truth, these two names are associated with this idea, which had only a philanthropic object in view: to save from the scourge of lead poisoning the unfortunate white lead workers, who, owing to the as yet still primitive methods of manufacture of that epoch, were continuously liable to lead poisoning by the white lead dust, which was very abundant in all white lead factories.

The enormous difference in cost which existed between zinc oxide, which then sold at 8 francs the pound (8 *livres la livre*), whilst white lead did not reach a quarter that sum, caused the efforts of these two philanthropists to come to grief, and it was not until half a century afterwards that a painter of Paris, John Leclaire, again took the matter up, and, after numerous experiments, was able to mix zinc oxide with oil, to form a paste capable of serving as a base in painting. This base did not dry sufficiently well. John Leclaire invented the process of boiling linseed oil with manganese dioxide, which yielded him an oil which dried as well as the boiled oil then in use, which was litharge-boiled oil. He thus replaced the lead

compound by a harmless one, and the oil rendered siccative by this method, added to paint with a zinc oxide basis, was made to dry very rapidly.

Principal of an important firm of Paris painters, a firm, moreover, which is still in existence, John Leclair used zinc oxide very extensively in his numerous undertakings. As he was a very clever craftsman, he knew how to make an excellent use of the new material, and it may be said that it is to him that we owe the definite introduction of zinc white into painting, the use of which increases every day.

#### PREPARATION OF OXIDE OF ZINC FROM THE METAL.

Zinc oxide, at the present day, is prepared by two different methods: (1) *from metallic zinc*; (2) *from zinc ores*. The second, a comparatively new process, is but little used in Europe. On the other hand, it has assumed a great development in the United States. It enables comparatively poor ores to be utilised, and furnishes an excellent yield. America, therefore, exports large quantities of this product into Europe, which is known in commerce under the designation of *American zinc white*, or *American zinc oxide*.

The preparation of zinc oxide from the metal is very simple. Its principles will only be recalled very briefly. All chemical treatises give this manufacture in all its details. Metallic zinc is distilled in crucibles, or retorts, and brought to the temperature of distillation, the metal becoming inflamed by contact with the air, produces the oxide. Moreover, it may be added that it is almost impossible to melt zinc without producing the oxide.

The retorts in which the metal is distilled are of refractory clay, with generally the following inside dimensions:—length, 1 to 1·4 metres; width, 35 centimetres; depth, 10 centimetres. Their sides are more or less thick, according to the nature of the refractory earth of which the retorts are constructed.



These retorts, closed at one end, have a rectangular opening at the other, 24 centimetres wide by 4 centimetres high; it is through this orifice that the retorts are charged with the metal, in ingots, and it is by the same orifice that the metallic vapours escape.

The general plan of the furnaces used for the distillation of zinc comprises a furnace, formed by a grate, 3 metres long, above which, to right and to left, are placed groups of two superimposed retorts, installed in such a way that the flame of the furnace can lick the sides. Each group of retorts is separated from its neighbour by a refractory partition. Often the furnaces are placed in juxtaposition by their end, and a single chimney placed in the centre serves both. Each of these furnaces comprises up to as many as 10 groups of 2 retorts, say, 20 in all, or 40 when the furnace has a double grate.

The front of the retorts, that is to say, the orifice, ends in a special piece constructed of refractory earth called the *guérite* (literally, sentinel's box), into which the metallic vapours pass as soon as they issue. This *guérite*, which is vertical, ends underneath in a flue, bringing atmospheric air intended for the combustion of the zinc above; it ends above in a wrought-iron pipe, through which the vapours pass, which are drawn to it by a draught chimney, placed at the end of the apparatus.

The wrought-iron pipe itself ends in what they call a coil, and which itself also consists of a series of wrought-iron pipes, in the shape of several successive V's, in which a first separation of the vapours converted into oxide is effected. At the bottom of each V a hopper is fixed, leading these products to special receivers. As they issue from the cooling tubes or coils, the fumes penetrate into depositing chambers, and their temperature then ought not to exceed 50° C. The depositing chambers generally comprise eight to nine vertical chambers, each one of which being divided into two equal parts by a partition, which, rising from below, does not reach quite to the top, it

follows that the vapours, passing into the interior of the chamber, rise vertically, glide over the top of the partition, redescend on the other side of the partition, penetrate from below into the next chamber, where they follow the same course, and so on, up to the last, which ends in the draught chimney, from which it is separated by tight wire gauze intended to arrest all the particles which the current of air might draw into the chimney. The path thus imposed on the metallic vapours attains a length of about 850 metres, and ensures the complete deposition of all the oxide which is produced.

It has been mentioned that the cooling tubes were provided with hoppers, intended to collect the condensed products. It must be added that, in the first tubes, hardly anything but metallic zinc dust is collected, then, further on, this same product, mixed with a little oxide, the mass in its entirety showing a grey tint. This product, ground in oil, forms a stone grey, or a slate grey of very good quality. Further on still, the same mixture is found, but much more rich in oxide, which is itself pure enough. Finally, in the depositing chambers, only zinc oxide is collected. The whitest and the lightest in density is deposited in the part nearest the draught chimney, the other chambers furnish zinc oxide, of greater and greater density, in proportion as they recede farther from the draught chimney, but of which the shade remains, even in the case of the most dense, of a very pure white.

Commercially, zinc oxides are distinguished thus: the lightest, and consequently the most white, bears the name of snow white, then come No. 1, No. 2, and No. 3, then commence the greys, which form more or less numerous brands, according to the factory. It may at once be said that snow white is very little used in painting. It is only used for fine paints in tubes; its most considerable outlet is in perfumery, in the manufacture of rice powders, face powders, and other products.

House decoration only utilises Nos. 1, 2, and 3. With a furnace of 40 retorts, 27 tons of zinc can be distilled in twenty-four hours, with the consumption of about 12 tons of coal. The theoretical yield indicates that 100 lbs. of zinc ought to produce 125 lbs. of zinc oxide, but, in practice, the furnaces give a yield of 5 to 10 per cent. less than theory.

It will be seen by the above that the consumption of fuel reaches 40 to 45 kilogrammes per 100 kilogrammes of metal heated; also that all the improvements, in this method of manufacturing zinc oxide, have been brought to bear on the system of furnaces with the view of reducing the coal bill.

It must further be mentioned very white oxides of zinc are only obtained by the use of very pure metal, and that old zinc always containing solder and consequently lead, which would soil the zinc oxide, should be rejected. Some manufacturers have, however, been enabled to use old zincs, by causing them to undergo a previous process of refining. Cadmiferous zincs ought to be rejected, as they impart to the oxide a very distinctive yellow coloration.

#### PREPARATION OF ZINC OXIDE FROM THE ORE.

The manufacture of zinc oxide from the ore being much more recent, and less known than that which has just been recalled, it will be described with a few more details.

It is to Wetherill to whom this process, which has undergone some modifications in details since its conception, is due, but the principles of which are always the same.

The course of this process may be summed up thus—

1. Reduction and volatilisation of the zinc at high temperature.
2. Reoxidation of the metal in the state of vapour, at a slightly higher temperature.
3. Cooling of the gases and condensation of the zinc oxide.

The reduction and volatilisation is effected in a furnace of a very simple form, and which consists of a semicircular arch resting on two uprights; the inside is divided horizontally into two parts by a grate which leaves above, under the keystone of the arch, the same height as underneath; the first of these serves as the furnace, the second as the ashpit.

The grate deserves special mention on account of its peculiar shape. Designed by Wetherill, the inventor of the process, it consists of iron plates 25 to 38 millimetres thick, pierced with conical holes, of which the upper diameter varies from 6·3 millimetres to 1 centimetre, and the lower is 2·5 centimetres. These holes are uniformly distributed at the rate of 100 per 1·075 sq. metre (?square foot). These plates are real firebars, because their length is equal to that of the furnace, for a width of 15 centimetres. They are retained transversely by lintels or narrow iron bars, so as not to obstruct the holes, their number is therefore relatively large generally, 16 per row of plates. It has been attempted to replace these plates by bars which almost fit into each other, analogous to the bars of the grate of the furnace, but the author understands that the results have not been very satisfactory.

The width of the furnace, or at least of the arched flue, is somewhat variable; in the beginning it was made 90 centimetres, then it was brought to 1·5 metre, and at the present time it is 1·2 metre, this last dimension appearing the best. As regards the length, it remains somewhat uniform, and fixed at 1·05 metre; however, it is sometimes extended to 3 metres, but then the furnaces are each provided with a door, at each extremity, instead of one only, at one of the ends, as in the four courts. It has been, moreover, attempted to increase this length, by bringing it to 4·85 metres, but working became defective.

The ashpit, which has a depth under the grate of 50 centimetres, is closed by a cast-iron door, which is only opened

once a day, to remove the residues, which have sifted through the grate. If it be logical, in order to handle the latter, to throw water into the ashpit, such a course is bad for the manufacture, steam is produced, which cools the furnace, and is an obstacle to the exhaustion of the ore being treated.

Through orifices, placed in the side walls of the ashpit, air is blown in, under the grate, at a pressure of 5 to 10 millimetres of water.

The arch itself communicates by an opening in its centre, with a sort of flue which extends the whole of its length. It is into this that the vapours disengaged above the grate first pass. It has been tried to use the heat of the sides of this flue to heat the injection air, which was made to circulate round about it. Such a procedure was a rational one, and yielded good results; on the other hand, it enormously complicated the carrying out of repairs, and was finally abandoned. It has, up to now, been said that the arch constituted the furnace; it would have been more correct to say that it formed one section of the furnace, because the apparatus, as a whole, comprises a larger or smaller number of these arches in juxtaposition, and all identical with that just described.

The reoxidation of the zinc vapours is produced in the same apparatus, owing to the space that these find above the charge which covers the grate and the flue on the top of the arch, a space which is at a very high temperature; however, according to the nature of the mineral treated, this reoxidation may be incomplete, and it is necessary to see that the vapours are not again cooled as they issue from the furnace, properly so called, that is to say, on their entrance into the top flue. When this occurs, the zinc oxide is greyish, whether from zinc dust or coal dust. In many installations this inconvenience has been obviated by making fireclay arches above the furnace proper, leaving between them two chambers which the gas traverses in a serpentine fashion; this principle, it will be seen,

is intended to maintain the temperature of the disengaged vapours.

It has also been attempted to convey the vapours into wrought-iron pipes rising to a certain height above the furnace, and ending, in another pipe, likewise of wrought-iron, parallel with the axis of the furnace, and acting as a collector. This system, in reality a very simple one, has the disadvantage of yielding defective products.

To sum up, the different improvements brought to bear on the Wetherill furnace have never given very satisfactory results, outside of those the object of which was only more complete utilisation of the fuel employed.

When the vapours have been kept at a high temperature, to ensure their oxidation, it is necessary to condense the fumes, and to precipitate the dust which they produce, which constitute the desired oxide of zinc. Now this condensation or precipitation, experience proves, is not accomplished well unless the vapours are sufficiently cooled, the more so as an ever-extending use is being made of cotton or woollen jackets, which present surfaces to the oxide of zinc, to which it has a greater natural tendency to adhere than to the smooth walls of a chamber, and which retain in a more persistent manner the finer particles, which form the lightest and the whitest oxide, and consequently the one which users are most desirous of obtaining. It will be seen, therefore, that the use of these fabrics is not compatible, unless the temperature be comparatively low, say,  $50^{\circ}$  C. ( $122^{\circ}$  F.).

In American factories this question of initial cooling of the vapours does not seem much trouble to manufacturers, who generally lead the insufficiently cooled zinc vapours into too large chambers. In certain European factories, where the Wetherill process is at work, it has been endeavoured, on the contrary, to substitute for the chambers, cooling pipes, from which the oxide passes to depositing chambers, as in the manufacture

of zinc oxide from the metal. This solution appears perfectly rational, provided sufficient capacity be given to these coolers.

The following is a description, according to Lodin (*Metallurgie du Zinc*, A. Lodin, Ingénieur en chef des mines), of how the plant has been installed at South Bethlehem, which has served as a type for the greater number of American factories:—From a bench of Wetherill furnaces the vapours—kept hot—issue through vertical wrought-iron pipes, which are collected together into one large pipe, also of wrought-iron, fixed horizontal above the bench of furnaces. It is as they issue from this collector that the vapours are cooled. To accomplish this, they first pass into a comparatively low tower; entering by the top, they descend towards the bottom, where there is an aperture which conveys them to a second tower, 7·5 metres in diameter and 21 metres high. The vapours circulate in this second tower from bottom to top, and in its upper part pass by two pipes of 1·8 metre, which descend parallel with the tower, and at the bottom of each of which a fan is fixed, which propels the cold vapours into the depositing chambers. The latter built of masonry are 30 metres long, 6 metres wide, and their available height is 7 metres. In the axis of their upper part, and extending all their length, runs a large wrought-iron pipe, from which pipes of less diameter branch off on either side. Each of these branch pipes comprises two tubulures, turned towards the ground, to which are fastened cotton jackets, ending in receiving vessels. Filtration is effected through these jackets, which are beaten at intervals by wooden sticks; two succeeding branch pipes are enclosed by a partition, which divides the chamber into as many small compartments as there are pairs of branch pipes. These compartments must be carefully ventilated when the jackets are being beaten, so as to avoid the initial stages of asphyxia, which the workers would suffer in an atmosphere supercharged with very fine dust.

The use of the fan to aspirate the vapours has the advantage

of causing such a depression in the furnaces as to render blowing unnecessary. On the other hand, its working is handicapped when the vapours have a temperature below  $100^{\circ}$  C., for then the steam from the ore, and the fuel even, if that always be coke or anthracite, condense and agglomerate the zinc oxide dust, which collect on the sides of the fan and stop it from working. This inconvenience is easily remedied, it is true, by fixing the fan in the spot, in the circuit of the vapours, where the temperature does not fall below  $100^{\circ}$  C. ( $212^{\circ}$  F.) or by two fans. When the first is obstructed, a damper enables the second to be brought into use, and the first cleaned.

The grading of the products is done, as in the old way of making zinc oxide, the whitest and the lightest are to be found at the end of the circuit.

The routine of the work is as follows :—The treatment of a charge lasts six hours. The work is graduated, from hour to hour, so as to form a continuous system of working.

When starting an operation, the grate is well cleaned with the rake, the sides of the furnace are brought to a bright red, a layer of non-bituminous fuel is thrown on the grate, coke or anthracite of the size of a nut. It is generally allowed that the weight of lighting fuel varies from 40 to 45 per cent. of the ore treated, the latter being normally 60 to 65 kilogrammes per square metre of grate surface. The thickness of the layer of fuel is about 3 centimetres, with anthracite, and double that with coke.

The thickness of the fuel which takes fire almost instantaneously by radiation from the walls of the furnace is rapidly made uniform. The door is closed, and it is given the draught or "wind," regulated by a damper; when all the layer is in active ignition, an intimate mixture of the ore in the form of grains, and coal, slightly moistened, is projected on its surface, the weight of the coal representing 40 to 50 per cent. of the ore,



It has been tried to increase the thickness of the layer by bringing it up to 35 and even to 45 centimetres, but the results obtained were bad, for the residue then contained 10 to 13 per cent. of zinc, even although the operation had been prolonged twelve to twenty-four hours. The mixture once charged, and evenly spread, say, about an hour, or an hour and a half, from the time the furnace was cleaned out, the working door is hermetically sealed, by piling against it the ashes and the clinkers, and the pressure of the draught is gradually increased, for three to four hours. The disengagement of zinciferous vapours first increase in a progressive manner, then diminish afterwards. When it has almost ceased, the blower is stopped, and the operation is finished. The grate is cleaned out with the rake, preserving the residuum, which may be treated specially. Lodin defines, in the following terms, the chemical reaction, which occurs in the preparation of zinc oxide, by the Wetherill process:—

“The inversion of equilibrium, induced by a lowering of temperature, on a mixture containing zinc vapours, carbonic oxide, and carbonic acid, is a phenomenon which constantly intervenes in the metallurgical treatment of zinc, the consequence is that dusts are produced which are less abundant in the case of reduction in closed vessels, but become absolutely predominant in reduction by the arched furnace. This inversion of equilibrium can, by itself, sufficiently explain the mechanism of the Wetherill process.

“In reality, it is not at the expense of the  $\text{CO}_2$  that the reoxidation of the volatilised metallic zinc is effected. The thickness of the layer of substances on the grate would not be sufficient to transform the oxygen of the wind into carbonic oxide, even if that layer were composed completely of fuel. Now the ore predominates there, and the fuel is too dense, to rapidly react on the oxygen. The wind, on the other hand, traverses the charge at a considerable speed. It can therefore be foreseen that the gaseous products of the reaction, in

addition to nitrogen and a little steam, only contain carbonic acid and oxygen to the exclusion of carbonic oxide.

"Experience confirms this way of looking at the subject. I have had occasion to make some analyses of gases taken from the working part of the Wetherill furnace, and found therein an excess of oxygen during all the phases of treatment. This excess is comparatively small in the beginning of the operation, when blowing is not so energetic; it may then be reduced to about 2 per cent. It increases gradually, towards the end of the operation, in proportion as blowing comes more energetic, and the temperature increases; it is then 7 to 12 per cent. It is higher when wind is directly introduced into the working part of the furnace than when blowing is confined to the ashpit.

"An insufficient excess of oxygen generally produces a more or less grey white.

"Secondary admissions of air are sometimes made in the working part of the furnace, sometimes in the collector above the furnace, when there is one."

As in manufacturing zinc oxide from the metal, the purity and whiteness of the product obtained by the Wetherill process depends on the quality of the ore.

When the ore contains lead, the lead is to a great extent volatilised with the zinc, and is afterwards found in the state of carbonate, sulphate, and oxide.

Silver is still more obnoxious than lead, as, even when the zinciferous ore only contains 100 grammes to the ton, the zinc oxide assumes a very decided grey tint. Arsenic and antimony are equally bad, but colour the white less than lead and silver.

As regards iron, opinions are divided; apparently the iron does not volatilise, and is not entrained by the oxide of zinc produced which would appear to confirm the long practice of certain American firms, whose product is absolutely free

from iron. Nevertheless, some brands of zinc oxide, manufactured by the Wetherill process, reveal on analyses appreciable quantities of iron.

Although it would be very difficult to say exactly what the ores are that are treated, because a mixture of ores from different sources is always taken, yet it is known that some United States factories use Franklinite, Wilhelmitite, and a little zincite, these different minerals entering into the mixture in variable proportion.

The treatment of a ton of this mixture requires 100 to 130 kilogrammes (2 to 3 cwts.) of coal; a workman can treat 120 kilogrammes (264 lbs.) of ore per hour, but, as the working of the furnace is somewhat laborious, the same man cannot stand it longer than eight hours, the cost of labour is therefore got by saying that a ton of ore requires the labour of two workmen's days. As stated in the beginning, the Wetherill process is only applicable to poor ores, and, moreover, ores of a certain quality, which would appear to explain why this process is only developed in America, where such poor ores exist. In Europe, where ores, testing up to 45 and even 50 per cent. of zinc, are treated, the Wetherill process requires a very protracted length of time for an operation, which increases the working expenses very considerably.

Besides the fact that zinc oxide, directly extracted from the ore, has not got the brilliant whiteness of that produced from the metal, and that that is due to its molecular condition, as already stated, it has, moreover, a much more feeble apparent density. Numerous apparent density tests made by the author on the two oxides, as delivered to the trade in pressed casks, have always given, for the first, a density of 0.800, whilst the density of the second was always above 1. This difference is again to be attributed, in the author's opinion, to the different molecular condition of the two products.

## CHAPTER VIII.

### GRINDING OF ZINC WHITE TO A STIFF PAINT IN OIL.

**Z**INC oxide, intended for painting, is delivered as a stiff paste in oil. This oil is poppy seed oil, when the product is intended for use on very particular work requiring perfect whiteness. Linseed oil is substituted for poppy seed oil when the paint is to be used on general work.

The preparation of this paste could not be more simple, it comprises two operations : (1) mixing ; (2) grinding.

Mixing is done in mixers analogous to those used in white lead factories. They ought, however, to be considerably more capacious, because zinc oxide is run into them in the form of a dry powder of an apparent density of 1.0, whereas the paste in oil presents a density varying from 2.5 to 3 according to the amount of oil incorporated. Poppy seed oil or linseed oil is run into the mixer pug mill, and the mixer started, and in order to yield an intimate mixture fit to pass through the rolls is kept at work for at least an hour.

The word "mixture" has been used advisedly by the author, for it is very decidedly and very clearly established that the two bodies zinc oxide and oil have no affinity for each other, and that no combination occurs between them ; therefore the whole secret in obtaining a good paste consists in effecting the most perfect mixing of the two bodies in question.

From the fact that the paste to be obtained is only a mere mixture, the relative quantities of the two substances to be brought in contact is essentially variable ; when the mixing

is done with poppy seed oil from 75 to 80 parts by weight of zinc oxide is used to 25 to 20 parts by weight of oil. According as the oil enters in larger or smaller quantity, the paste obtained is less or more compact, and its density is less or greater. The greater the percentage of oil, the more prompt is the mixing; and conversely, when mixing is done with linseed oil, the proportion of oil should be reduced. The mixings most generally used are 80 up to 83 of zinc oxide, and 20 down to 17 of oil. The advantage of using linseed oil is that it gives a better drying paint than poppy seed oil, but this difference in drying is exclusively due to the nature of the oil.

When mixing is finished, which is known by the mixer yielding quite a homogeneous product, the paste is passed through rolls identical with those used for white lead manufacture.

The greater the length of time the mixing has been prolonged, the quicker can be the passage through the rolls. In the early days of this manufacture, the paste issuing from the mixer passed successively into three sets of rolls in which the rolls were gradually set closer and closer. But, it must be added, that at that time grinding was done exclusively in poppy seed oil, with which several passages through the rolls in succession have no bad effect. With linseed oil, especially old tanked oil, repeated grindings tend to render the paste tacky (stringy). In order to remedy this it was proposed to add 1 to 3 per cent. of water, but this plan has never given good results, because if it prevented stringing for the time being, it yielded a product which rapidly hardened and often solidified in bulk. Nowadays, therefore, it is preferred to prolong the mixing and only pass the paste once through the rolls.

Too prolonged mixing has also its defects, and never yields a good product. As to the cause of this inferiority of the resulting product, opinions are divided; it seems to the author,

judging from his own experience, that it is to be found in the heat, sometimes rather considerable, to which the paste is exposed, especially when the mixer is continuously at work for a whole day. The heat produced by the friction of the parts of the mixer in motion, added to that of the molecules of oxide, the one against the other, tend to deteriorate the oil, or at least to modify its original nature by the production of secondary products, the presence of which in the paste has the most bad effect. Some test experiments, made by intentionally heating the mixers on the one hand, or cooling them on the other, have shown that better results were obtained by cooling than by heating the mixer.

Going beyond the question of the consistency of the paste which it is desired to obtain, which regulates the amount of oil to be mixed with the oxide, it must be remarked that the lower the apparent density of a zinc oxide falls, the more oil it requires to form a paste of a predetermined consistency. Thus, for the same manufacture, snow white will absorb more oil than No. 1 white, the latter more than No. 2. This is also why zinc oxide made from the metal, being more dense than that extracted from the ore, takes less oil than the latter in grinding. All grinders are, moreover, agreed on that point, and find that American zinc oxide requires more oil to bring it to the same form of paste than zinc oxide made from the metal. Livache, who has occupied himself greatly with painters' materials, has even determined that the fact is not peculiar to zinc oxide, but is generalised for all pulverulent powders, which caused him to enunciate the following law: "The amount of oil should increase in proportion as the density of the solid matter diminishes, and for two substances of different densities, the quantities of oil ought to be in inverse ratio to the densities." This law is almost exact in this sense, that it is necessary to understand, by density, the weight of a determined volume of the products concerned. If, for example,

we take barium sulphate, it is known that its volume will be more bulky the weaker the liquors by which its precipitation has been effected. Now this is always barium sulphate, the absolute density of which is ever the same, but the molecular condition of which is different. If, therefore, barium sulphate, precipitated in concentrated liquors, yields a product with a greater apparent density than that of the same product in dilute liquors, the former will require less oil to convert them into a paste of given consistency than the second. It is necessary, therefore, in interpreting Livache's law, to read the word "density" as the *apparent density* of the product.

As it issues from the rolls, the paste of zinc oxide is fit for delivery to consumers. This delivery is always in zinc tins, or in tinned iron vessels hermetically closed by a soldered lid. The tin is itself packed in a wooden receptacle, which is simply a cask of white wood with staves which fit more or less exactly, and in which no endeavour is made to make it water-tight, but merely a protecting envelope for the tin, generally made of excessively thin metal. It is usual, in the French zinc white stiff paint trade, to include, in the net weight of the product, the weight of the metal; the wooden envelope alone constitutes the tare deducted from the gross weight.

Zinc white stiff paint must never be packed in wooden casks, that material being capable of absorbing the oil, which has such a great tendency to separate from the product, and in a very short time the latter would be deteriorated.

When it is desired to preserve zinc white stiff paint in a newly opened receptacle, or in one that is in use, the surface of the product is covered with a slight layer of oil.

## CHAPTER IX.

### ZINC WHITE PAINT AND ZINC WHITE COATINGS— THEIR MERITS AND DEFECTS.

**Z**INC white stiff paints are treated absolutely in the same way as white lead stiff paints. That is to say, the desired colour is added to the zinc white pastes in oil, then a mixture of linseed oil, spirits of turpentine, and of liquid or solid dryer, so as to bring the paint to the desired fluidity for application.

To make zinc white putty, or filler, the zinc white is never used pure, but finely pulverised and sifted Paris white is added to it. The proportions in which the Paris white enters vary according to the ideas of the craftsman, but it ought to be said that they are always rather high, stiff zinc white paint, ground in oil alone, lending itself very badly to the making of putty, or fillers.

The properties of zinc white paints and putties, or fillers, are those of zinc white itself, which possesses an inalterable whiteness and communicates quite a peculiar freshness to the paints of which it forms the basis; besides, if noxious ingredients have not been added to the zinc white paste in oil, its use is absolutely harmless.

As to the defects which are very justly urged against zinc white, and the paint made from it, they are numerous enough. Zinc white covers poorly. It dries poorly. It stands the weather badly.



It is once more to Stas to whom we must refer for an explanation of these defects. Speaking of zinc white he expresses himself thus:—

“Let us see what takes place when zinc white and oil are mixed, and when such a paint is exposed to dry, applied on an object. The zinc white suspends itself in the oil, but however long may be the duration of the contact of these two substances, whether there be presence or absence of air, whether the oil be fresh or recent, *under no circumstances whatever does any appreciable quantity of the zinc oxide dissolve in the oil.*”

“If water be made to intervene, and the contact between the oil and the white be prolonged, whilst slightly elevating the temperature, a very small quantity of the oil saponifies; the linoleate and the margarate of zinc, products which dissolve in the oil whilst hot, *never remain dissolved in the oil after cooling.* By directly bringing linoleate and margarate of zinc in presence of oil at a high temperature, these zinc salts dissolve in greater or less amount, but separate entirely out on cooling to such an extent that the oil, in this case, scarcely contains more than two parts in a thousand of zinc oxide in solution. Thus, as far as regards the circumstances in which paint is made and used, it may be said that zinc oxide as well as zinc linoleate and zinc margarate are insoluble in linseed oil.

“Linseed oil, which has been in presence of zinc oxide, and in which linoleate of zinc has been dissolved, dries no better than linseed oil, before its contact with these substances.

“By mixing linseed oil, zinc oxide, and borate of manganese, and abandoning this mixture for several days, in contact with air, the oil decomposes borate of manganese, and dissolves the protoxide of that metal. That oil may thus take up as much as 2 per cent. of that metal, it forms a liquid with a feeble yellow colour, which, left in contact with air, oxidises very rapidly and precipitates sesquioxide of manganese, which

colours the solid matter intensely brown. Under such circumstances no trace of zinc oxide is dissolved in the oil.

“The linoleate and the margarate of the protoxide of manganese are very soluble in linseed oil, the solution, which is colourless, becomes blood red in contact with air. In this condition it dries rapidly, and communicates this property to linseed oil. It dries to a red transparent varnish.

“If we deduce from the preceding facts what ought to occur in the preparation and the drying of zinc white paint, and the chemical nature of the coat after drying, we arrive at the following result:—Painting made with the help of a dryer contains, as has been said, traces of linoleate and margarate of manganese, the oil solidifies, enveloping the particles of zinc white, but the solid substance produced, only containing traces of manganese soap, presents the properties of linseed oil, which has been made to dry after incorporating an inert body therewith. As the oxide of zinc does not dissolve in oil, the traces of manganese which it has been found possible to dissolve therein, have simply rendered it siccative, and on the drying of this paint it only consists of zinc oxide, a covering body, mechanically interposed in oxidised linseed oil.

“Has water been made to intervene during the grinding of the paint? In that case, the zinc oxide interposed in the dried oil may be mixed with a certain quantity of linoleate and margarate of zinc, but these salts remain, like the zinc oxide itself, outside the substance of the oxygenated oil, because they were insoluble in the oil, in the conditions in which the paint was applied.

“Zinc white paint, therefore, can form a coat in no way whatever more durable than any other paint obtained by mixing oil with an inert matter.”

The author will not discuss the terms, sometimes inexact, in which this savant tells us of his examination of zinc white

paints. But he retains the fundamental principle of it, which is perfectly exact. Zinc oxide, mixed with poppy seed or linseed oil, enters into no combination with either, and it is only the mixture of an inert solid substance, zinc oxide, with a liquid substance, oil, a mixture of which the constituent principles, in virtue of their great difference in density, only tend to separate. The proof of this is demonstrated every day. Let one, in fact, open a vessel containing stiff zinc white paint in oil, and the oil will be seen to swim about on the top in a more or less thick layer; if the stiff paint is old, the whole of the oil is on the top, and the whole of the zinc oxide at the bottom, however well the mixing and grinding have been executed.

The poor covering power of zinc white is explained by that simple fact, for in the case of a coat of zinc white paint, the same separation is produced on the surface, which is covered by it, and the coat of paint will show the juxtaposition of solid opaque molecules, and of transparent liquid molecules. To sum up, it will form on the surface a real canvas enabling one to perceive through its meshes the paint underneath it.

The poor drying capacity of zinc white is very clearly explained by Stas. The zinc oxide, forming no combination with the oil, imparts to it no new property, and its drying power remains what it was when it existed by itself, that is to say, comparatively poor.

Finally, the want of durability is also explained by the same cause. The absence of combination, leading to the separation of the elements of the paint, zinc oxide, and oil. The oil in drying forms a varnish on the inert pulverulent body, that is, on the oxide of zinc, but the resistance of this varnish is known to be very poor, besides its depth is exceedingly thin, and it is rapidly worn away by rain, by dust, and by the wind, etc.

It would seem that owing to the absence of the qualities

required in a basis for good paint, zinc white should be excluded from the latter. That is not so, and very fortunately, for the craftsman has accustomed himself to remedy matters in different ways.

As regards the poor covering power of zinc white, that is obviated by applying several coats in succession. The second coat barely covers the transparent parts, the third and the succeeding ones complete the gaps which may have been produced. This great number of superimposed coats increases the labour, and consequently the cost of the painting which has been executed, but it is useful to state that painting done in zinc white is considered as a job to be done in a particularly careful manner with the custom acquired long since of regarding it as a more costly transaction.

The defective drying power of zinc white paint can be very much attenuated by adding solid or liquid driers to the paint. The author will not say that this is as good as if the paint dried naturally. But this method enables the execution of a certain class of work to be accelerated, and the time thus economised is often worth the sacrifice of a little of the intrinsic quality of the work.

Finally, the want of resistance to atmospheric agents of zinc white, or of the paints of which it forms the base being perfectly well recognised, this product is excluded from all outdoor work, and there remains for it a very great position in indoor work where its resistance suffices.

To sum up, if zinc white has defects, which are in some ways fundamental defects, from a pictorial point of view, it has great properties, as regards the obtaining of effects, in virtue of its inalterable whiteness, and the freshness which it respects in bright tints. Thus in all indoor work where either a very pure white is desired or fresh bright tones, pure zinc white is used, either alone, or as the basis for making the paints.

The author, however, thinks that zinc oxide suitably treated

in grinding might very well produce a compound presenting all the properties which it now lacks. The author's own protracted personal researches on this point have convinced him that zinc oxide can, like lead compounds, yield with oil, and particularly with linseed oil, real chemical compounds forming fatty salts of zinc, which correspond absolutely with the conditions formulated by Stas, and which he found only to occur with white lead.

It is to be well understood, however, that it is necessary for that purpose to modify the current methods of grinding, and to lose sight entirely of that idea recognised as false, a long time before our day, and to recognise that it is not enough to make a stiff paste ground in oil capable of serving as a basis for paint, by simply mixing as intimately as possible a white pulverulent powder with oil, so as to obtain a greasy unctuous paste. What is necessary is to endeavour to obtain the possible (chemical) combination of these products. It was on these lines that the author pursued his researches, when applying himself to find the means of combining zinc oxide with oil. This combination not being capable of being brought about directly, and zinc oxide being a very well-defined body, its properties cannot be changed, it was towards the oil that the author directed his attention. After having examined all the oils of which the painter might make a judicious use, the author stopped short at linseed oil. In virtue of its property of an organic body, this oil is capable of undergoing most profound modifications. It is known, in fact, that linseed oil exposed to the air oxidises, and becomes very drying (the linoleic acid is transformed into oxylinoleic acid); that oil heated gently to a medium temperature may likewise gain in drying; that heated rapidly to a high temperature, it thickens, and loses all its drying properties.

Therefore, by treating linseed oil specially, it is possible to make from it a body having quite a peculiar affinity for oxide

of zinc. The author has thus been able to obtain zinc white pastes in oil, of marked drying properties, covering power, and resistance. Stiff zinc white paint so prepared never separates from the oil; exposed to the air, it covers itself with a skin and is preserved indefinitely, under a layer of water. The author has profited by these special properties by applying his paste in oil, to make steam joints, gas joints, water joints, etc., which are now done with white lead.

Pushing his researches still further, he has found that ferric oxide, sesquioxide of chromium, and other metallic oxides may likewise form fatty compounds, soluble in oil, or in a mixture of oil and spirits of turpentine, and serve as rational basis in industrial paints.

Even with an experience more than secular, one should not entirely condemn zinc white, because the author is assured that the defects which it exhibits at the present time are solely due to the fact that sufficient effort has not been made to make from it with oil a well-defined compound such as those furnished by white lead and lead oxides.

There, the author believes, is a programme which merits the attention of chemists more competent than himself; and then the trade will be in possession of real substitutes not only for white lead, but for many other articles, the use of which is justifiably regarded as injurious to the health of the workmen. Then there will be no need of promulgating laws to suppress the use of such and such a colour, the craftsman having the choice between two good products, will choose the one which exposes him to the least danger.

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